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Crestmoreite and riversideite.

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A. Introduction.

THESE two minerals were described by Eakle[2] from the crystalline limestone at Crestmore, Riverside County, California. Both were shown to be hydrated monocalcium silicates, containing small amounts of P_2O_5, SO_3, and CO_2, occurred with a fibrous habit, and had closely similar optical properties. They were distinguished chiefly by the higher water content (approx. 1·3 mol.) of crestmoreite as compared with riversideite (0·5 mol.), and by the fact that the former was included directly in the calcite, whereas the latter formed veins in masses of idocrase which were contained in it. The minerals had been produced under hydrothermal conditions caused by igneous intrusions. In both cases, the primary material was believed to have been wilkeite, which is an apatite mineral with much of the phosphorus replaced by sulphur, silicon, and possibly carbon. Due to the fibrous nature of both minerals, optical determinations are difficult; data are given by Eakle, Larsen,[3] and Fairbanks.[4]

Flint and co-workers[5] investigated one specimen of crestmoreite, and two described as riversideite, by X-ray powder photographs. They

[1] Now at Department of Chemistry, University of Aberdeen.

[2] A. S. Eakle, Bull. Dept. Geol. Univ. California, 1917, vol. 10, no. 19, p. 327. [M.A. 1–20.]

[3] E. S. Larsen, Bull. U.S. Geol. Surv., 1921, no. 679, p. 280. [M.A. 1–367.]

[4] E. E. Fairbanks, *in* Winchell, Optical mineralogy. 2nd edit., 1927, p. 227; 4th edit., 1951, p. 421.

[5] E. P. Flint, H. F. McMurdie, and L. S. Wells, Journ. Res. Nat. Bur. Stand. U.S.A., 1938, vol. 21, p. 617. [M.A. 7–283.] H. F. McMurdie and E. P. Flint, ibid., 1943, vol. 31, p. 225. [M.A. 9–45.]

found that the crestmoreite gave a characteristic pattern, and that one specimen described as riversideite was identical with the crestmoreite, whereas the other was in reality foshagite. They also found, contrary to Eakle's results, that most of the water in crestmoreite in excess of that present in riversideite was lost at 110°, and that this did not alter the X-ray pattern. They concluded that riversideite was not a distinct species, and proposed that the name be dropped. Clark and Bunn[1] also obtained X-ray data for riversideite, which differ slightly from those of McMurdie and Flint. Data close to those in Clark and Bunn's paper are given on card II–1298 of the American Society for Testing Materials.[2]

Although a number of other hydrated calcium silicate minerals have been synthesized, material has never been obtained in the laboratory giving an X-ray pattern and optical data identical with those of natural crestmoreite or riversideite. Alcock, Clark, and Thurston[3] found, however, that a boiler scale gave an X-ray pattern similar to that of crestmoreite.

Nomenclature.—The suggestion that the name riversideite be discarded in favour of crestmoreite has met with general acceptance, and the latter name has therefore been adopted in the following account. The name tobermorite is used for the mineral discovered by Heddle[4] and for the artificial product, 'calcium silicate hydrate (I)',[5] which has been found[6] to be substantially identical with it. It has been shown[7] that this substance exists in several distinct states of hydration, which do not differ fundamentally from each other in crystal structure; and, pending the adoption of agreed nomenclature for the separate hydration states, the name tobermorite is used broadly to include all of them without further particularization.

B. Examination of crestmoreite.

1. *Material.*

A specimen labelled 'riversideite' (B.M. 1921,101) was made available by courtesy of the Trustees of the British Museum, and two others, also

[1] L. M. Clark and C. W. Bunn, Journ. Soc. Chem. Indust., 1940, vol. 59, p. 155. [M.A. **8**–116.]

[2] American Society for Testing Materials, first supplement to card file of X-ray diffraction data, 1944; from data supplied by Imperial Chemical Industries, Northwich, England.

[3] T. C. Alcock, L. M. Clark, and E. F. Thurston, Journ. Soc. Chem. Indust., 1944, vol. 63, p. 292. [M.A. **9**–103.] L. M. Clark, Min. Mag., 1948, vol. 28, p. 362.

[4] M. F. Heddle, Min. Mag., 1880, vol. 4, p. 119.

[5] H. F. W. Taylor, Journ. Chem. Soc. London, 1950, p. 3682. [M.A. **11**–314.]

[6] G. F. Claringbull and M. H. Hey, Min. Mag., 1952, vol. 29, p. 960.

[7] H. F. W. Taylor, Journ. Chem. Soc. London, 1953, p. 163. [M.A. **12**–172.]

labelled 'riversideite', were kindly supplied by Professor A. Pabst from Eakle's original collection at California University. In each case the material was soft, white, and fibrous in accordance with Eakle's description. The British Museum specimen was supplied free from adjacent minerals, although microscopic and X-ray single-crystal investigation revealed the presence of minute traces of idocrase, and of a second fibrous species which could not be identified; rotation photographs showed that the repeat distance along the fibre axis of the latter was 6·86 Å. The crestmoreite in the two specimens from Eakle's collection was present as veins a few millimetres thick. These were of irregular shape, and the fibres of which they were composed only remained parallel over small regions. Idocrase, diopside, calcite, and wollastonite were present in close proximity to each other and to the crestmoreite.

2. *Optical examination.*

All three specimens broke down, on rough crushing, into flakes which were apparently composed of approximately parallel fibres. Unless very thin, they were almost opaque, and only incomplete optical data could be obtained. Flakes from any of the specimens, when lying on the principal cleavage, had mean refractive indices within the range 1·59–1·60, with very low birefringence. Extinction was uneven, but always broadly parallel to the fibre direction. Some flakes had positive elongation and others negative elongation; the latter was observed chiefly in the case of flakes from either of the specimens from Eakle's collection. Satisfactory observations could not be made on flakes in other orientations. These results agree with those given by Eakle, except for the signs of elongation, which he states to be positive for both crestmoreite and riversideite.

3. *X-ray powder investigation.*

X-ray powder photographs were taken of each of the crestmoreite specimens, using cameras of 6 cm. and 19 cm. diameter with Cu-$K\alpha$ radiation. The results (table I) are in substantial agreement with those of earlier investigators. Agreement is best with the data on card II–1298 of the A.S.T.M. index, and worst with those of McMurdie and Flint, but there can be little doubt that in every case the same substance was being examined.

A comparison with photographs of wilkeite and of synthetic 'calcium silicate hydrate (I)' (table I) shows that, with certain minor exceptions, all the crestmoreite lines can be accounted for, if this substance is a

TABLE I. X-ray data for synthetic tobermorite, crestmoreite, and wilkeite. Spacings in Å.

Synthetic tobermorite.[1]	Specimen labelled 'Riversideite' (B.M. 1921,101).	Specimen labelled 'Riversideite' (Eakle's collection).	Wilkeite (B.M. 1914,1129).[2]
—	14·0 vs	14·0 s	—
11 s	11·2 mw	11·2 w	—
—	8·2 mw	8·2 m	8·2 mw
5·6 ms	5·6 m	5·6 mw	—
—	—	—	5·1 vw
—	4·7 w	—	—
—	—	4·1 vvw	4·1 vw
—	3·90 vvw	3·90 vw	3·90 vw
3·55 vvw	3·73 vw	—	—
—	3·45 ms	3·45 ms	3·45 ms
3·28 vvw	3·25 mw	—	—
—	—	—	3·16 vw
3·07 vvs	3·07 vs	3·07 ms	3·07 vw
2·97 s	2·97 s	2·97 mw	—
2·80 s	2·80 vvs	2·81 vvs	2·82 vs 2·79 ms
—	2·72 vs	2·72 vs	2·72 s
—	2·62 m	2·62 ms	2·62 ms
2·52 vw	—	—	—
2·48 vw	—	—	—
2·28 ms	2·29 ms	2·29 mw	—
—	2·27 m	2·27 ms	2·27 ms
2·15 m	2·15 mw	2·15 w	2·15 w
2·07 m	2·07 s	2·07 w	2·07 vw
—	—	2·03 vw	2·03 vvw
2·00 m	2·00 mw	2·00 vw	2·00 vw
1·93 vvw	1·94 s	1·94 vs	1·94 ms
—	1·88 w	1·88 vw	1·88 m
1·83 vs	1·83 vs	1·83 vs	1·83 s
1·81 vvw	1·80 mw	1·80 ms	1·80 mw
—	1·77 w	1·77 m	1·77 mw
1·76 vvw	—	—	—
—	1·74 w	1·74 m	1·74 mw
1·71 vvw	1·71 mw	1·71 ms	1·71 m
1·67 s	1·67 ms	1·67 w	—
—	1·63 vw	1·63 mw	1·63 w

[1] Sample 58, of approximate composition $CaSiO_3,H_2O$, prepared by L. Heller and H. F. W. Taylor (Journ. Chem. Soc. London, 1951, p. 2397; 1952, p. 1018. [M.A. 11–471]), and described there as 'calcium silicate hydrate (I)'. The data in column 1 are slightly more accurate than those given in the original paper, and are the same as those quoted by Claringbull and Hey (1952).

[2] Data separately determined for a specimen of wilkeite.

Relative intensities: s = strong, m = moderate, w = weak, v = very, d = diffuse.

TABLE I (*continued*).

Synthetic tobermorite.	'Riversideite' (B.M. 1921,101).	'Riversideite' (Eakle's collection).	Wilkeite (B.M. 1914,1129).
1·61 vw	1·61 vw	1·61 vvw	1·61 w
1·59 vvw	—	—	—
1·53 m	1·53 w/d	1·53 w/d	—
—	1·50 w	1·50 mw	1·50 w
—	1·47 w	1·47 m	1·47 mw
—	1·45 mw	1·45 m	1·45 m
1·43 vw	1·43 mw	1·43 m	1·43 mw
1·405 w 1·395 w	1·40 w/d	1·40 mw	—
1·370 vvw	—	—	—
—	—	1·36 vw	1·36 vvw
—	1·33 vw	1·33 vw	1·33 vw
—	1·32 vw	1·32 vw	1·32 vvw
—	1·28 vw	1·28 vw	1·28 vvw
1·260 vvw	1·26 vw	1·26 vw	1·26 w
—	1·24 w	1·24 w	1·24 w
1·225 vw	1·23 vw	1·23 w	1·23 vw
1·185 vvw	1·180 vvw	—	—
1·160 vvw	1·155 vw	1·155 vw	1·155 vw
—	1·145 vw	1·145 vw	1·145 vw
—	1·135 vvw	1·135 vvw	1·135 vvw
—	1·115 vw	1·115 vw	1·115 vw
—	1·105 vw	1·105 vvw	1·105 w
1·110 w	1·100 vw	1·100 w	—
1·075 vw	1·075 vw	—	—

mixture of tobermorite and wilkeite. The proportion of the latter constituent appears to be lower in the British Museum specimen than in the two specimens from Eakle's collection, which gave almost identical photographs.

4. *X-ray single-crystal investigation.*

Rotation and zero-layer Weissenberg photographs (figs. 1 and 2 respectively) were taken about the fibre axis of a flake from the British Museum specimen. They show two distinct and superimposed patterns, viz.:

(i) A pattern of relatively sharp spots, which could be indexed on a hexagonal cell having a 9·45±0·05, c 6·90±0·05 Å. The c-axis was parallel to the fibre direction. These conclusions were confirmed by taking oscillation photographs about c and a, a first-layer Weissenberg photograph about c, and a Laue photograph with the X-ray beam parallel to c. The parameters obtained agree with those found by

McConnell[1] for wilkeite (a 9·48, c 6·91 and a 9·40, c 6·89 Å. for specimens containing respectively 14·4 and 32·2 % of P_2O_5). Comparison of the photographs with corresponding ones of wilkeite (B.M. 1914,1129) showed close agreement as regards intensities of corresponding reflections.

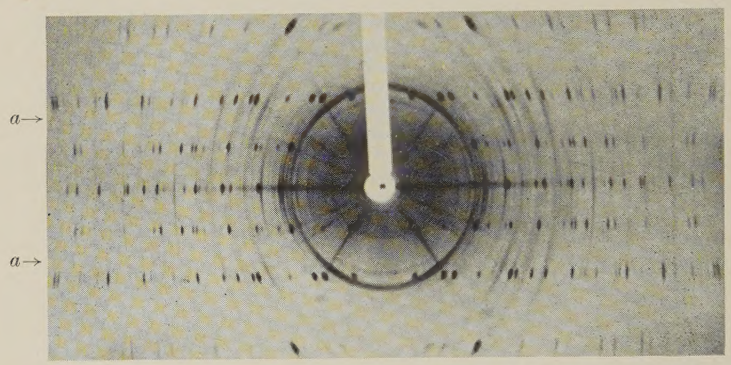

Fig. 1. X-ray photograph of crestmoreite (B.M. 1921,101). Rotation about the fibre axis. a,a: second layer-line of the tobermorite constituent.

(ii) A preferred orientation pattern, consisting of arcs in the oscillation and rotation photographs (fig. 1), and of streaks in the Weissenberg photographs (fig. 2). Direct comparison showed that this preferred orientation pattern, as seen in the oscillation and rotation photographs, was in substantial agreement with the powder pattern of synthetic tobermorite (fig. 3), although certain discrepancies were observed which corresponded with those noted in connexion with the powder investigation. It has been shown elsewhere (Taylor, 1953, loc. cit.) that variations

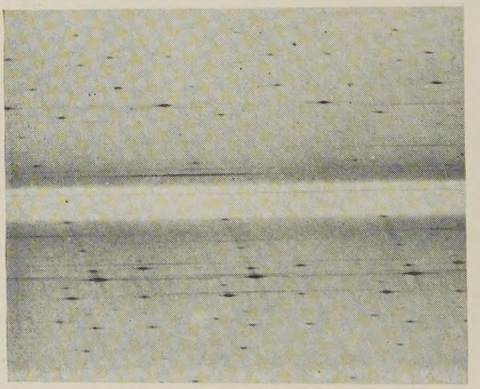

Fig. 2. X-ray photograph of crestmoreite (B.M. 1921,101). Zero-layer Weissenberg about the fibre axis.

[1] D. McConnell, Amer. Min., 1937, vol. 22, p. 977. [M.A. 7–14.]

in the X-ray pattern of 'calcium silicate hydrate (I)' are caused by differences in the hydration state, and inspection of the photographs showed that this provided a satisfactory explanation of the dis-

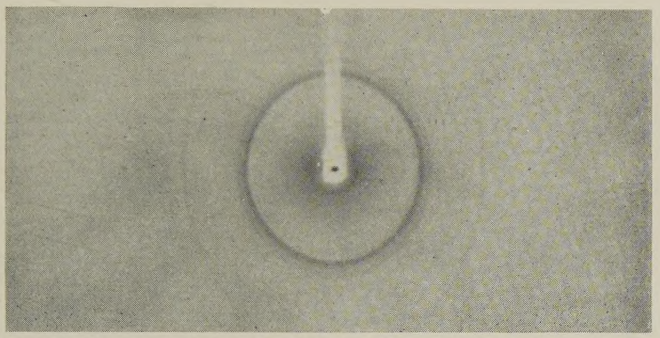

FIG. 3. X-ray powder photograph of synthetic tobermorite (specimen for which data are listed in table I).

crepancies in the present case. The preferred orientation patterns showed a repeat distance in the *b*- or fibre direction of 7·30 Å. The odd layer-lines on rotation about this axis are very weak, and cannot be seen in the reproduction (fig. 1).

5. *Qualitative mineral composition.*

The effects described above might be ascribed to the chance association of crystals, or fibres, of the two minerals. However, certain facts exclude this explanation. Twelve crystals, taken from different parts of all three specimens, and varying in size from under 100 μ to 800 μ in length, were studied, and in all cases the same effect was observed. The *c*-axis of the wilkeite, the fibre direction, and the mean direction of the crestmoreite *b*-axis always coincided. Among crystals from any one specimen no significant differences could be observed either in the relative intensities of the two patterns, or in the degree of orientation of the crestmoreite, although, in accordance with the powder data, the British Museum specimen appeared to be richer in the latter constituent than were those from Eakle's collection. Finally, no crystals of wilkeite were visible under the microscope.

The only possible explanation is that the flakes are very close intergrowths of crestmoreite and wilkeite. This probably accounts for their opacity, a characteristic that was observed by Eakle. The individual regions occupied by the two minerals are apparently sub-microscopic, and ordinary methods of separation are likely to be impracticable.

6. *Chemical analysis.*

The results of a chemical analysis of one of the specimens (labelled 'riversideite') from Eakle's collection are given in table II, column 1.

TABLE II. Chemical analyses of crestmoreite.

	1.	2.	3.	4.	5.	6.
SiO_2	27·4	3·0	35·3	1·00	38·30	1·00
TiO_2	< 0·1	—	< 0·1	< 0·002	—	—
Al_2O_3	0·9	—	1·3	0·02	—	—
Fe_2O_3	0·3	—	0·4	0·005	—	—
MgO	1·0	—	1·4	0·06	—	—
CaO	48·8	11·3	48·2	1·46	41·20	0·97
P_2O_5	4·9	4·9	—	—	3·50	—
SO_3	4·0	4·0	—	—	1·25	—
CO_2	3·3	—	—	—	—	—
$H_2O(110°)$	3·7					
$H_2O(450°)$	5·1	—	13·3	1·26	15·17	1·35
$H_2O(1000°)$	0·4					
	99·9	23·2	100·0		99·42	

1. Crestmoreite, Crestmore, California, from A. S. Eakle's collection. Analyst, F. J. McConnell, on 0·47 gm. Sp. gr., 2·45. Total iron as Fe_2O_3. H_2O loss at 110° under water-vapour pressure 6 mm. to reach equilibrium; at 450° also at 6 mm.; at 1000°, loss after deduction of CO_2.

2. Oxides allocated to wilkeite.

3. Column 1 after deduction of wilkeite (23·2 %) and calcite (7·5 %), and calculated to 100%.

4. Molecular ratios calculated from column 3.

5. One of three closely agreeing analyses of crestmoreite (A. S. Eakle, 1917). Eakle also gave an analysis of riversideite, as do Clark and Bunn (1940), whose results, however, show that the material analysed was really crestmoreite.

6. Molecular ratios from column 5 after deducting wilkeite.

Portions of this material had been used in the X-ray work already described. The material had been carefully selected, fibre by fibre, under the microscope, and except for a small proportion of calcite, no other minerals could be detected. In order to interpret the results, it was necessary to correct for the presence of the wilkeite, and as the composition of this mineral is very variable, this could only be done approximately. It was assumed that the wilkeite contained all the P_2O_5 and SO_3, together with amounts of CaO and SiO_2 required by the formula $3Ca_3(Si,P,S)_2O_8.CaO$. By allowing for the oxides thus allocated to wilkeite (column 2), and deducting also CO_2 as calcite, an approximate estimate of the composition of the hydrated calcium silicate was obtained (columns 3 and 4). For comparison, one of Eakle's three analyses of

crestmoreite is included, together with the molar ratios calculated from it on the assumption that the P_2O_5 and SO_3 are present as wilkeite (columns 5 and 6).

Due to the assumptions which have to be made, it would be wrong to place too much reliance on these results. They nevertheless support the conclusion reached from the X-ray work, that the specimen contains wilkeite together with a hydrated calcium silicate, and suggest further that this has a composition comparable to that of Eakle's crestmoreite.

C. Examination of specimens labelled 'crestmoreite'.

Two specimens labelled 'crestmoreite' were examined. One (B.M. 1919,2) was from the British Museum collection, and the other, supplied by courtesy of Professor A. Pabst, was from Eakle's original collection. Both consisted of inclusions of soft, white, fibrous material in blue calcite, in agreement with the original description. X-ray powder and single-crystal photographs showed, however, that both consisted mainly of an apatite mineral, with unit-cell dimensions near to those of wilkeite. This was confirmed by chemical analysis in the case of the specimen from Eakle's collection, which consisted of a mixture of calcite and wilkeite.

X-ray single-crystal photographs of the British Museum specimen showed, in addition to the strong pattern of spots characteristic of the apatite mineral, a number of weak powder-lines. The spacings and relative intensities of these showed a general resemblance to those of the micas and other minerals containing $(Si_2O_5)_n$ sheets of hexagonal type. A small proportion of a second species was thus present, unoriented and intergrown with wilkeite. Insufficient material was available for analysis, and it was not therefore possible to establish whether this species was a hydrated calcium silicate; but this might be considered unlikely, in view of the fact that the calcium ion is apparently too large to occupy the octahedral positions in structures of this type.

D. Discussion.

The present results show that all three of the specimens labelled 'riversideite' were sub-microscopic intergrowths of tobermorite and wilkeite. The X-ray powder data for these specimens are in agreement with those found for 'crestmoreite' by Flint, McMurdie, and Wells, and with those found for 'riversideite' by the same investigators and by Clark and Bunn. Hence, if the two specimens labelled 'crestmoreite' that were examined in the present investigation can be discounted, all

specimens described as crestmoreite or riversideite for which X-ray data are available have been composed of tobermorite and wilkeite. It is probable that in all cases the two constituents were intergrown in the same way, as any coarser mixture could hardly have escaped detection.

The appearance of the hand-specimens, the optical properties, and the chemical analyses (given by Clark and Bunn and in the present investigation) are sufficient to establish that all the above specimens consisted of essentially the same material as the crestmoreite and riversideite originally examined by Eakle. All the evidence is thus consistent with the view that the specimens from the Crestmore locality, which have been called crestmoreite or riversideite, are sub-microscopic intergrowths of tobermorite and wilkeite.

Some observations on the state of hydration of the crestmoreite in one of the specimens described here have been reported elsewhere.[1] They showed that the crestmoreite was a mixture of two hydration states having water contents of approximately 2·5 and 1·0 molecules respectively. Further examination now in progress suggests that a small proportion of the hemihydrate is probably also present and that still other hydrates may also exist in the material. The crestmoreite in the intergrowths from Crestmore is thus a complex mixture as regards hydration state, and it is reasonable to conclude that the differences between the water contents of various specimens, including Eakle's original crestmoreite and riversideite, are due to differences in the relative proportions of the several hydrates present.

Due to the presence of wilkeite, the optical and X-ray data which have been attributed to crestmoreite differ appreciably from those of pure tobermorite, as found (in the case of natural material) by Claringbull and Hey. This accounts for the fact that attempts to synthesize material with properties similar to those attributed to crestmoreite have not succeeded, since in all cases the starting materials have contained only lime, silica, and water. On the other hand, tobermorite is readily obtained in the laboratory under hydrothermal conditions,[2] and its formation at Crestmore may therefore be understood. Alcock, Clark, and Thurston's observation that a boiler scale gave an X-ray pattern similar to that of crestmoreite may also be explained, since a mixture of

[1] H. F. W. Taylor, Journ. Chem. Soc. London, 1953, p. 165. [M.A. **12**–172.] The specimen was of crestmoreite from A. S. Eakle's collection, labelled 'riversideite', by which name it was (incorrectly) described in that paper.

[2] L. Heller and H. F. W. Taylor, Journ. Chem. Soc. London, 1951, p. 2397; 1952, pp. 1018, 2535. [M.A. **11**–471, **12**–83.]

tobermorite and some apatite mineral could well have been formed in the scale. This mixture would give an X-ray powder pattern similar to that of crestmoreite.

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The unit cell and space-group of chlor-spodiosite (Ca_2PO_4Cl).

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[Communicated by Dr. J. W. Jeffery; taken as read January 22, 1953.]

As part of a study of the structure of whitlockite (β-$Ca_3(PO_4)_2$) attempts were made to prepare single crystals of the mineral synthetically.[1] At 1180° there is a polymorphic transition from the rhombohedral β-form to a high-temperature monoclinic form α-$Ca_3(PO_4)_2$.[2] The density of the α-form is 12% less than that of the β-form and large crystals were not found to transform without powdering. $CaCl_2$ was therefore added as a flux to see whether crystals of $Ca_3(PO_4)_2$ could be produced from a melt below 1180°. The melting point of pure $Ca_3(PO_4)_2$ is about 1800°. In addition to chlorapatite ($Ca_5(PO_4)_3Cl$), a phase of composition Ca_2PO_4Cl was produced. This compound had been earlier observed by Cameron and McCaughey,[3] who identified the crystals as being closely related to the mineral spodiosite (Ca_2PO_4F).[4] A report[5] that spodiosite was identical with apatite appears to have been based on a specimen of altered material which was a pseudomorph of apatite after some unknown mineral. X-ray powder photographs of chlor-spodiosite and apatite are quite distinct.

The synthetic crystals were orthorhombic and exhibited the same forms, {001}, {110}, {010}, as described by Tiberg, Nordenskiöld,[6] and Cameron and McCaughey. (110):($1\bar{1}0$) was about 82° and flattening with the predominance of (001) was usually marked. Crystals were sometimes flattened on to (110). The hopper formation of many crystals was most striking.

[1] A. L. Mackay, Ph.D. Thesis, London University, 1952.

[2] M. A. Bredig, H. H. Franck, and H. Fuldner, Zeits. Electrochem., 1933, vol. 39, p. 959. [M.A. 6–57.]

[3] F. K. Cameron and W. J. McCaughey, Journ. Phys. Chem., 1911, vol. 15, p. 463.

[4] H. V. Tiberg, Geol. För. Förh. Stockholm, 1872, vol. 1, p. 84.

[5] H. Strunz, Naturwiss., 1939, vol. 27, p. 423. [M.A. 7–494.]

[6] G. Nordenskiöld, Geol. För. Förh. Stockholm, 1893, vol. 15, p. 460.

The refractive indices were found to be α $1{\cdot}65_0$, β $1{\cdot}66_3$, γ $1{\cdot}67_0$. The acute and obtuse bisectrix figures confirmed the negative optic sign; 2V $75° \pm 5°$ (measured). The optic orientation is $\alpha = b$, $\beta = a$, $\gamma = c$. Larsen[1] gives the indices α 1·663, β 1·674, γ 1·699 with the optic sign positive for the natural spodiosite (Ca_2PO_4F).

Cameron and McCaughey give the refractive indices of chlor-spodiosite as α 1·649, β 1·665, γ 1·670 and state that the birefringence is positive, that c is the acute bisectrix and that a is the obtuse bisectrix. They also say that the prism angle $(110):(1\bar{1}0)$ is 82°, presumably implying that $(110):(1\bar{1}0) = 98°$ (the a and b axes are interchanged with respect to those used in this paper). It will be observed that their optic sign is inconsistent with their refractive indices and appears to have been determined from the obtuse bisectrix figure. If this is so, then their optical properties agree with those found by the present author.

From precession camera photographs the unit-cell dimensions were measured as a 6·17, b 6·89, c 10·74 Å. Using the measured density of 3·03 g./c.c. (Cameron and McCaughey, 3·041) the calculated number Z of formula units per cell is $3{\cdot}95_0 \simeq 4$. Extinctions in the X-ray pattern are characteristic of the diffraction symbol $P2/b\,2_1/c\,2_1/m$. The space-group is therefore probably $Pbcm$ or $Pca2_1$. As a Giebe-Scheibe test for piezoelectricity gave negative results the centred group $Pbcm$ is to be preferred. From goniometric measurements Nordenskiöld obtained for the axial ratios of natural spodiosite $a:b:c = 0{\cdot}893:1:1{\cdot}584$. The X-ray measurements above give $0{\cdot}896:1:1{\cdot}559$ as the corresponding values for the chlor-spodiosite, confirming the similarity of the two varieties.

These orthorhombic cell dimensions provide some justification for the inclusion by Dana of spodiosite in the wagnerite group. Wagnerite itself (Mg_2PO_4F) is monoclinic with space-group $P2_1/c$ and has dimensions a 11·90, b 12·51, c 9·63 kX, β 108° 07′; Z 16 and a density of about 3·07–3·14 g./c.c. Mg may be replaced by ferrous iron or Mn, F by OH, and P by As, altering the dimensions and density slightly. As these substitutions are possible, it would seem that the structure has considerable stability and probably remains substantially unchanged when Ca and Cl are introduced, although these ions are somewhat larger than the corresponding ions in wagnerite. It will be noted that the a and b dimensions of wagnerite are nearly twice those of chlor-spodiosite and the c dimension is slightly less, while Z is correspondingly

[1] E. S. Larsen, Bull. U.S. Geol. Surv., 1921, no. 679, pp. 136, 223.

four times as large. It is plausible that the increase in the size of the ions may simplify the structure. There is also a resemblance to the orthorhombic members of the olivenite ($Cu_2(AsO_4)(OH)$) and descloizite ($Pb(Zn,Cu)VO_4(OH)$) groups. No members of these groups containing chlorine ions are known, so that very close relationships are not necessarily expected.

The author is grateful to Mr. C. G. A. Hill for the sample of synthetic chlor-spodiosite. The work described is in part included in a thesis approved by the University of London.

The structures of the plagioclase felspars: III. An X-ray study of anorthites and bytownites.

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1. Introduction.

In a recent paper, Cole, Sörum, and Taylor[1] described X-ray measurements on a number of plagioclases with compositions ranging from pure albite to pure anorthite. As a result, they were able to make more precise, and extend, the structural interpretations proposed on the basis of earlier X-ray investigations of the three type-structures, albite, anorthite, and intermediate plagioclases (Taylor, Darbyshire, and Strunz;[2] Chao and Taylor[3]). At the same time, new complexities were revealed which called for more detailed examination, among them the fact that the anorthite-type structure, with *c*-axis ~14 A., may have either a body-centred or a primitive unit cell. The body-centred cell was observed with a material containing 71·5% anorthite, the primitive cell with a nearly pure anorthite, but there was not sufficient evidence to show whether the difference was due entirely or largely to the difference in chemical composition, nor was a detailed investigation made of the effects of heat-treatments. The work now to be described was undertaken in the first place in order to clarify these aspects of the plagioclase problem.

It has however become clear, as the experimental data have accumulated, that, quite apart from any structural interpretation which may be proposed, the observed small differences in the X-ray single-crystal patterns may provide a direct method of supplying the petrographer with information, which could not easily be obtained otherwise, on the

[1] W. F. Cole, H. Sörum, and W. H. Taylor, Acta Cryst., 1951, vol. 4, p. 20. [M.A. **11**–427.]

[2] W. H. Taylor, J. A. Darbyshire, and H. Strunz, Zeits. Krist., 1934, vol. 87, p. 464. [M.A. **6**–177.]

[3] S. H. Chao and W. H. Taylor, Proc. Roy. Soc. London, Ser. A, 1940, vol. 176, p. 76. [M.A. **8**–13.]

geological thermal history of the samples. The present paper is concerned with this aspect of the research; its bearing on the problem of the atomic structure of anorthite will be discussed elsewhere.

The potential importance of the X-ray method becomes clear when the results of optical examination of the plagioclases are considered. Köhler's[1] interpretation of his optical data in terms of high-temperature and low-temperature series of plagioclases was followed by the researches of Tertsch,[2] van der Kaaden,[3] and others. In a critical review of the optical data Reynolds[4] concludes that while there is a marked difference between the high-temperature and low-temperature forms from Ab_{100} to $Ab_{65}An_{35}$, and a significant distinction may still be made in the range $Ab_{65}An_{35}$ to $Ab_{30}An_{70}$, from $Ab_{30}An_{70}$ to An_{100} no certain differentiation into two series can be established by optical measurements. The familiar and convenient methods which are so powerful for soda-rich plagioclases thus become increasingly ineffective for the lime-rich bytownites and anorthites.

2. Experimental data.

Twelve specimens have been examined in the range An_{100} to $An_{70}Ab_{30}$. The second and third columns of table I give the place of origin, and the nature of the rock where this is known; the fourth and fifth columns give the anorthite-content and the method used to obtain the composition. Except for the two cases noted in the table (nos. 6 and 9), where universal-stage methods were used, the 'optical methods' depend upon refractive-index and extinction-angle measurements. It should be noted that if it is accepted that for this region of the plagioclase system the optical properties for high-temperature and low-temperature materials are nearly identical no serious uncertainty arises in estimating composition from these measurements.

All plagioclases have similar structures. The most obvious and characteristic feature of the anorthite-type structure is that while the a and b axes, and the α, β, γ angles, of the unit cell remain approximately the same as those of albite (a 8 Å., b 13 Å., $\alpha \sim 90°$, $\beta \sim 116°$, $\gamma \sim 90°$), the true c-axis is approximately 14 Å. in anorthite, the albite c-axis of 7 Å. being only a pseudo-repeat distance in anorthite. Thus,

[1] A. Köhler, Journ. Geol., 1949, vol. 57, p. 592. [M.A. **11**–144.]
[2] H. Tertsch, Tschermaks, Min. Petr. Mitt., 1941, vol. 53, p. 50. [M.A. **8**–313.]
[3] G. van der Kaaden, Thesis, Univ. Utrecht, 1951. [M.A. **11**–282.]
[4] D. L. Reynolds, Geol. Mag., 1952, vol. 89, p. 233. [M.A. **12**–137.]

in general, X-ray reflections of anorthite with l odd are weak by comparison with reflections with l even.

TABLE I. Bytownite and anorthite specimens.

Specimen no.	Locality.	Origin.	Anorthite content (Mol. %).	Method of determination.	Type (c) reflections.
1	Pasmeda Alp, Fassa Valley	Limestone block	~ 100	Optically	Present; sharp
2	Monte Somma, Vesuvius	Olivine-limestone block	~ 100	Optically	Present; sharp
3	—	Synthetic	100	—	Present; diffuse
4	Miyaké, Japan	Volcanic lava	99·1	Chemical analysis	Present; diffuse
5	Tarumaé, Japan	Volcanic lava (?)	95·5	Chemical analysis	Present; diffuse
6	Northern Province, Tanganyika	Zoisite-amphibolite	95–97	Optically (universal stage)	Present; sharp
7	Miyaké, Japan	Same as no. 4	~ 94	Optically	Present; diffuse
8	Grass Valley, California	Hornblende-norite	92·8	Chemical analysis	Present; sharp
9	Glen Harris, Rum	Allivalite	88–91	Optically (universal stage)	Present; diffuse
10	Juvenas, France	Eucrite (meteorite)	~ 88	Optically	Present; diffuse
11	St. Louis Co., Minnesota	Anorthosite	~ 80	Optically	Absent
12	Crystal Bay, Minnesota	Anorthosite	70·1	Chemical analysis	Absent

For the present purpose it is convenient to group all possible X-ray reflections into four classes (a), (b), (c), (d) in which for (a) $(h+k)$ is even, l even; for (b) $(h+k)$ is odd, l odd; for (c) $(h+k)$ is even, l odd; for (d) $(h+k)$ is odd, l even. Reflections of type (a) are common to all felspars and are, in the main, strong and sharp; (b) are relatively weak subsidiary reflections characteristic of the doubled c-axis of anorthite and given by all materials having the anorthite-type structure; types (c) and (d) are weak additional reflections the presence of which indicates that the true cell is primitive since (c) and (d) do not conform to the body-centring condition $(h+k+l$ even) satisfied by both (a) and (b). It is found that all reflections (b), (c), (d) may be diffuse by comparison with (a), though those of type (b) do not show the gross diffuseness which is sometimes observed in type (c); reflections of type (d)

are very few in number and it is uncertain whether they can exhibit extreme diffuseness. It will be seen, below, that it is primarily with reflections of type (c) that this work has been concerned.

Diffuse reflections may be seen in oscillation photographs, but moving-film methods are more convenient for their study, and for most of the materials examined zero- and third-layer Weissenberg photographs taken about the a-axis, with Cu-$K\alpha$ radiation, have been used: confirmatory photographs, with oscillation about other prominent

FIG. 1. Part of an oscillation photograph taken about the a-axis of a crystal of synthetic anorthite using Cu-$K\alpha$ radiation. The diffuse reflections present are marked with arrows.

crystallographic directions, have been obtained where necessary. Figs. 1 and 2 illustrate the appearance of reflections of the different types, in oscillation and Weissenberg photographs.

The last column of table I shows whether X-ray reflections indicating a primitive unit cell are seen, and if so, whether they are sharp or diffuse; these observations are discussed in detail below.

It should perhaps be made clear that the diffuseness of some reflections cannot be due to variation in composition over the crystal specimen: for all the fragments used were examined optically and showed no

signs of the 'zoning' which is frequently seen in plagioclases; the diffuseness is confined to reflections with indices of certain types only; and it is seen in synthetic pure anorthite.

3. Discussion of results.

All the materials so far examined give one or other of three diffraction patterns. In the first, (S), reflections (c) and (d) are present and sharp; in the second, (D), reflections (c) are present and diffuse, reflections (d) are absent or so weak as to be doubtful; in the third, (A), reflections (c) and (d) are absent.

Pattern S.—Specimen 1 gives a diffraction pattern of the first type. Reflections of all types (a), (b), (c), (d) are observed, and although reflections (b), (c), and (d) may be slightly diffuse by comparison with (a), the difference in sharpness—if any—is very slight. A large number of reflections (b) are observed, but there are relatively few reflections (c) and very few reflections (d).

The same diffraction pattern is given by specimen 2, an observation which confirms the work of Cole, Sörum, and Taylor, who reported this material as having a primitive unit cell. Fig. 2(*a*) shows part of a zero-layer *a*-axis Weissenberg photograph of specimen 2 in which reflections of types (a), (b), (c) are marked.

Fig. 2(*a*) Part of a zero-layer Weissenberg photograph taken about the *a*-axis of a crystal of an anorthite from Monte Somma, Vesuvius, using Cu-$K\alpha$ radiation. Typical reflections of types (a), (b), and (c) are marked.

Fig. 2(*b*) The corresponding part of a zero-layer Weissenberg photograph taken about the *a*-axis of a crystal of synthetic anorthite using Cu-$K\alpha$ radiation. It will be noted that the reflection marked (c) in fig. 2(*a*) is no longer present. Further, type (c) reflections denoted by arrows are diffuse; the corresponding reflections in fig. 2(*a*) are marked.

The patterns of specimens 6 and 8 are also similar, though some of

the reflections (b), (c), (d) may be slightly more diffuse than for specimens 1 and 2.

Pattern D. –Specimen 3 (synthetic pure anorthite) gives a strikingly different pattern: no significant changes are seen in reflections (a) and (b), all reflections (d) have disappeared, and the few remaining (c) reflections are *very* diffuse—so diffuse that they might easily be overlooked, in which case the structure would be described as body-centred. The diffuse reflections observed (notably 007, 0015, $0\bar{6}3$, $0\bar{4}3$, $0\bar{6}5$, 025, $0\bar{2}7$, $0\bar{4}5$, $0\bar{2}15$, $3\bar{1}5$) are elongated along the b^* direction. Fig. 2(*b*) shows a part of a Weissenberg photograph of specimen 3, corresponding to figure 2(*a*) for specimen 2.

Specimens 4, 5, 7, 9, 10 give similar diffraction patterns. The degree of diffuseness of corresponding reflections may vary slightly for the different specimens, though this is difficult to decide; thus for specimen 9 (Glen Harris, Rum) reflections (c) while still being very diffuse are probably not quite so 'smeared out' as those from specimen 3 (synthetic).

Pattern A.—Specimens 11 and 12 give only reflections (a) and (b), reflections (c) and (d) being completely absent; the unit cell is thus truly body-centred.

Some tentative conclusions[1] of a general character may be drawn from these observations, though they can only be regarded as provisional on account of the absence of precise information about the geological thermal history of the mineral specimens.

(i) For pure or nearly pure anorthites, the occurrence of diffuse reflections (D pattern) indicates a high temperature of formation followed by rapid cooling, while the S pattern indicates either a low temperature of formation or very slow cooling from a high temperature. Specimens 3, crystallized from about 1500° C. overnight, and 1, certainly of low-temperature origin, may be taken as typical examples.

The distinction is maintained from An_{100} to about $An_{93}Ab_7$, at least: for the D pattern is observed in specimens 4, 5, 7, which are from volcanic lavas, i.e. quenched from a high temperature, while the S pattern is given by specimens 6 (of low-temperature origin, most probably metamorphic or metasomatic) and 8 (plutonic, cooled slowly from a moderately high temperature).

[1] Some of these deductions are in accordance with results reported briefly by F. Laves and J. R. Goldsmith, in abstracts of papers to Amer. Cryst. Assoc. meeting, Chicago, 1951.

Specimen 2 is of special interest. In Cole, Sörum, and Taylor this material (B.M. 49465) is mistakenly (by reason of its place of origin—Monte Somma, Vesuvius, a classic locality for high-temperature sanidines) considered to be of high-temperature origin. Its occurrence in an olivine-limestone block makes it clear, however, that it is actually of low-temperature origin, probably being formed as a secondary product either by thermal metamorphism or metasomatism. In this connexion it is interesting to note that Monte Somma, Vesuvius, is also among the sources listed by Chaisson[1] for adularia, which is generally regarded as of low-temperature origin.

The X-ray pattern thus provides a direct means of distinguishing high-temperature and low-temperature types in the composition range An_{100} to $An_{93}Ab_7$.

(ii) As the proportion of soda-felspar increases, the distinction becomes less clear-cut. The change from the S pattern (in which sharp reflections (c) and (d) indicate a primitive cell) to the D pattern (in which the reflections are diffuse) represents a trend towards the A pattern in which these reflections have vanished, the cell being then body-centred. The occurrence of the A structure only, in specimens 11 and 12 and in a specimen $An_{71\cdot5}Ab_{28\cdot5}$ examined by Cole, Sörum, and Taylor (1951), suggests strongly that the presence of a considerable proportion of soda-felspar affects the symmetry, even of a low-temperature material, in the same way as raising the temperature of the nearly pure anorthite—i.e. in favouring the body-centred structure. For specimens 11 ($An_{80}Ab_{20}$) and 12 ($An_{70}Ab_{30}$), of plutonic origin, have cooled slowly from high temperatures and thus have thermal histories rather similar to that of specimen 8 ($An_{93}Ab_7$) which gives the S pattern. The specimen $An_{71\cdot5}Ab_{28\cdot5}$ is from Split Rock Point, Minnesota, and may have a similar thermal history, though definite information is, unfortunately, lacking.

It is thus suggested that diffuse reflections indicating an intermediate stage in the transition from a truly primitive to a truly body-centred anorthite-type cell may be observed *either* as a consequence of a high temperature of formation, followed by rapid cooling, *or* when a considerable proportion of soda-felspar is present, even if the material is of low-temperature origin or has been cooled very slowly from a higher temperature. It is also reasonable to assume, in the light of the observations recorded above, that the transition from primitive to body-centred structure is essentially continuous in character and does

[1] U. Chaisson, Journ. Geol., 1950, vol. 58, p. 537. [M.A. **11**–326.]

not occur suddenly at some particular composition or temperature—a point left undecided in the work of Cole, Sörum, and Taylor (1951).

It remains to consider specimens 9 and 10. Specimen 9, from a plutonic rock, has probably cooled slowly from a high temperature and so might be expected to give an S pattern such as is given by specimen 8. However, the presence of hornblende in association with felspar in that specimen probably indicates a lower initial temperature than for specimen 9, for which the initial temperature may be as high as those for the Japanese volcanic specimens 4, 5, and 7. In addition it is possible that the appearance of the D pattern may, in part at least, be due to the influence of the soda-felspar; in view of the uncertainty as to the precise chemical composition it is difficult to decide whether this is an important factor for this specimen.

The thermal history of specimen 10 is probably similar to that of specimen 9, except that 10 has probably been reheated, to a low temperature, as is shown by the metamorphic clouding of the felspar. Here the considerable proportion of soda-felspar ($\sim 88\%$ An) may well be an important influence in producing the structure to which the observed D pattern corresponds. Little weight can be given to the observations on the specimen, however, since P. M. Game (private communication, 1952) has shown that in this meteoritic material different grains have different optical properties.

4. Conclusions.

The experiments described in this paper establish a means of distinguishing high-temperature from low-temperature plagioclases when the soda-felspar content does not exceed about 7% (mol.). They also suggest that the transition from the primitive to the body-centred type of structure is continuous in character; the diffuse reflections observed with nearly pure anorthites of high-temperature origin indicate that in these materials the transition is incomplete; the truly body-centred structure is observed with plagioclases containing between 20% and 30% (mol.) of soda-felspar even after slow cooling.

In an investigation in which so little precise information on thermal history is available, all conclusions based on the examination of a rather limited number of specimens must be regarded as provisional. Further work is in hand.

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The effect of grinding on micas. I. Muscovite.

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[Taken as read March 26, 1953.]

IT has long been realized that grinding increases the cation-exchange capacity of minerals and that it damages their crystal structures. However, while a considerable amount of data has been accumulated with regard to the effect upon various minerals, and clay minerals in particular, very little is known about how micas behave and such results as are available are somewhat inconsistent (1, 2, 3). In view of this and of a fortuitous observation that short-period grinding in an agate mortar affected the nature of muscovite considerably, a more detailed study of this subject has been undertaken.

Experimental.

The muscovite used originated from Goshen, Massachusetts, and consisted of clear colourless sheets relatively free from inclusions. The

Table I. Chemical analyses of muscovite.

	A.	B.	C.
SiO_2	45·4	50·99	46·95
TiO_2	—	0·19	0·22
Al_2O_3	38·5	30·10	34·02
Fe_2O_3	—	2·54	2·63
MgO	—	0·61	0·30
CaO	—	0·07	2·23
Na_2O	—	0·54	0·33
K_2O	11·8	8·87	3·17
H_2O +105° C.	4·3	6·13	10·58
	100·0	100·04	100·43

A, Theoretical composition of muscovite, taken as $KAl_2(AlSi_3)O_{10}(OH)_2$.
B, Muscovite, Goshen, Massachusetts; filed, 200 mesh.
C, Muscovite, Goshen, Massachusetts; ground for 24 hours, 200 mesh.
Analysts: B. D. Mitchell and Miss E. S. Murdoch.

optical data were α 1·566, β 1·577, γ 1·580, 2V fairly large, compared with α 1·552, β 1·582, γ 1·588, 2V 47° for pure muscovite (4). The chemical analysis in table I (B), as compared with the theoretical, calculated from the formula $KAl_2(AlSi_3)O_{10}(OH)_2$, indicates that the amount of

substitution in the tetrahedral layer is hardly so high as the theoretical (cf. SiO_2, Al_2O_3, and K_2O), and that this material has a small iron content.

Since filing is known to be very much less destructive than grinding, one part of the sample was filed to pass through a 200-mesh sieve to give

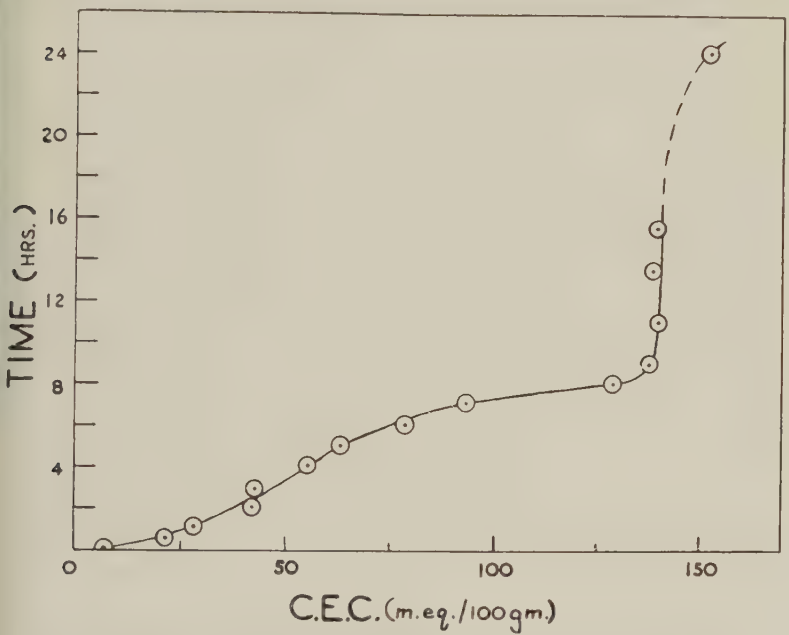

Fig. 1. Relationship between cation-exchange capacity and time of grinding for muscovite.

a powder of unaltered material, while the other part was dry-ground in a mechanical agate mortar, samples being removed at various times up to 24 hours and sieved through 200-mesh. For the X-ray diffraction photographs Fe-$K\alpha$ radiation was used; intensities were measured visually and estimated by comparison with the strongest line in the photograph. Differential thermal analysis was performed according to standard procedure using 0·20 g. samples (5). Semi-micro methods were employed for determination of chemical composition, of cation-exchange capacities (6), and of dehydration curves, which were obtained by weighing the material after heating it for one hour at temperatures increasing by 50° C.

Results and discussion.

The graph for variation in cation-exchange capacity (c.e.c.) with time of grinding (fig. 1) shows that although the c.e.c. of the filed material is

very low (about 6 milliequivalents/100 g.), that of the material ground for one hour is already almost 30 m.e./100 g. It would appear, therefore, that figures of this order quoted in the literature (7) probably arise from a somewhat similar period of grinding and are not necessarily equivalent to the value for the unaltered material. The c.e.c. increases

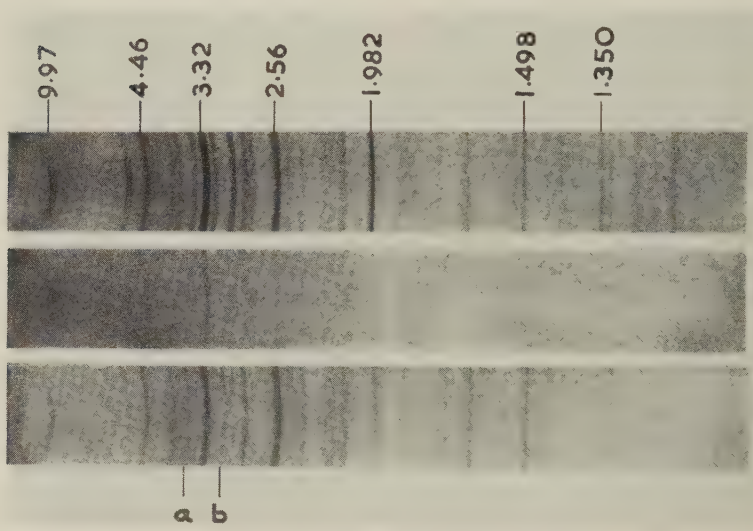

Fig. 2. X-ray diffraction patterns for muscovite samples:

A. Muscovite, Goshen, Massachusetts; filed, –200 mesh.
B. „ „ „ ground 8 hours, –200 mesh.
C. „ „ „ ground 24 hours, –200 mesh.

Fe-$K\alpha$ radiation; doubling of lines in A due to use of thick specimen with consequent specimen absorption: for details of *a* and *b* in C see text. (Spacings in Ångström units.)

steadily with time of grinding until about 7 hours and between 7 and 8 hours it increases more rapidly. Thereafter, up to about 18 hours, it remains fairly constant, but between 18 and 24 hours again increases slightly. The value obtained after 24 hours fits in with the value of 208 m.e./100 g. obtained by Jackson and Truog (2) after 72 hours grinding, but is considerably higher than the other published values, viz. 76 m.e./100 g. (Kelley and Jenny, 1), and about 100 m.e./100 g. (Parkert et al., 3). The reason for this is not clear as these three investigations were all performed using ball-mills—where the conditions are probably less drastic than in an agate mortar.

The sharp reflections observed on X-ray photographs of the filed material (fig. 2 A) gradually weaken in intensity and become more diffuse on grinding until, after 8 hours, no sharp reflections remain (fig. 2 B). After a further period a diffraction pattern reappears, but this is different from the original in that the lines have different intensities

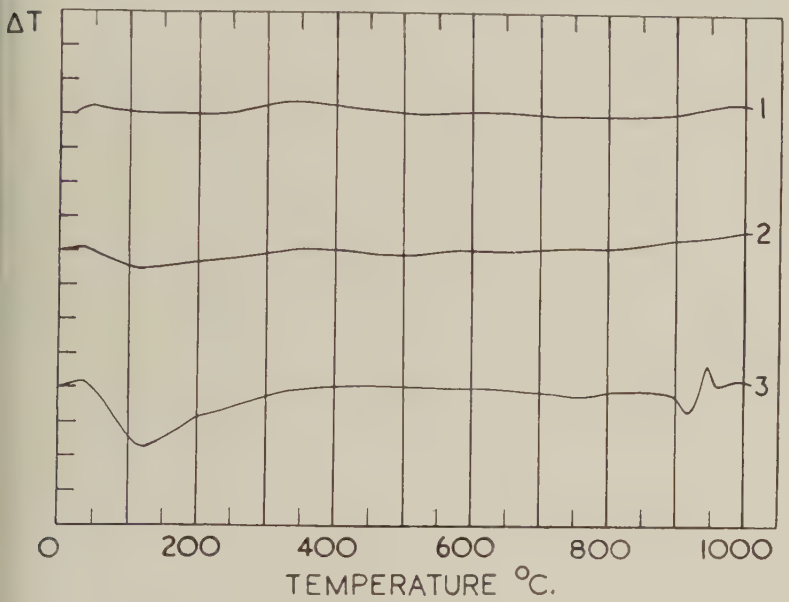

Fig. 3. Thermograms for muscovite: 1. Filed; 2. Ground for 2 hours; 3. Ground for 24 hours.

and there become visible two new lines which are not present in the muscovite pattern but which are given by many hydrous micas (8, 9, 10) viz. those at 3·59 and 3·09 Å. (*a* and *b*, fig. 2 C). The diffraction pattern does not alter with further grinding up to 24 hours. The X-ray patterns of unground and ground muscovite together with those for hydromuscovite (9) and for Ballater illite (10) are listed and indexed in table II, and those lines which show considerable change on grinding are indicated. It will be observed that, generally, (*hkl*) reflections are enhanced while reflections of the type (0*kl*) with $k = 2n$ decrease in intensity. The former effect might be expected, but the disappearance of the (0*kl*) lines remains to be explained. Glycerol treatment of the ground material did not alter the basal spacing.

The thermogram for filed muscovite (fig. 3) shows virtually no thermal

TABLE II. X-ray data.

Indices	Muscovite Goshen, Mass.		Hydromuscovite, Ogofau, Wales (9).		Muscovite Ground 24 hours.		Illite Ballater (10).	
	d.	Int.	*d*.	Int.	*d*.	Int.	*d*.	Int.
002	9·97	s	9·98	s	9·85	s	9·9	s
004	4·99	w	5·02	s	4·94	mw	4·9	m
110†	4·46	m	4·51	m	4·43	s	4·45	vs
111	—	—	—	—	—	—	4·28	w
022*	4·11	vw	—	—	—	—	4·10	w
11$\bar{3}$†	3·87	w	—	—	3·85	mw	3·87	m
023*	3·72	mw	3·62	s	—	—	3·64	mw
113†	—	—	—	—	3·59	mw	—	—
11$\bar{4}$	3·48	w	—	—	3·47	vw	—	—
006	3·32	vs	3·34	vs b	3·32	vs	3·35	vs
114	3·18	w	—	—	3·18	vw	—	—
11$\bar{5}$†	—	—	3·09	s	3·09	m	3·09	mw d
025*	2·98	mw	—	—	2·97	vw	—	—
115†	2·85	w	2·89	s	2·85	ms	2·85	md
11$\bar{6}$	2·78	w	—	—	2·78	vw	—	—
13$\bar{1}$, 200		—	—	—	2·59	vw	—	—
131, 20$\bar{2}$	2·56	ms	2·59	vs	2·55	s	2·56	vs
008, 13$\bar{3}$, 202 ...	2·46	vw d	2·47	m	2·44	w	2·45	mw
20$\bar{4}$, 133† ...	2·37	w	2·39	s	2·37	m	2·39	m
22$\bar{1}$	—	—	2·27		2·248	—	—	—
041*	2·24	vw	—	w	—	vw	2·235	mw
221, 22$\bar{3}$	2·19	vw	2·18		2·187	vw	—	—
20$\bar{6}$, 043, 135 ...	2·123	mw	2·135	s	2·126	m	2·14	m
044*	2·045	vw	—	—	—	—	—	—
0010*	1·982	s	1·994	vs	1·978	m	1·988	m
206†	—	—	—	—	1·953	vw	1·940	w
208†	1·722	vw	1·715	vw	1·712	vw	—	—
20$\bar{1}\bar{0}$, 312 ...	1·638	w	1·648	s	1·640	mw	1·647	m d
313	1·597	vw	—	—	1·612	vw	—	—
	—	—	—	—	1·575	vw	—	—
314	1·552	vw	—	—	1·546	vw	—	—
1310*	1·518	vw	—	—	—	—	—	—
060, 33$\bar{1}$	1·498	w	1·505	s	1·498	ms	1·497	s
331	1·451	vw	—	—	—	—	—	—
0014*	1·410	vw	1·416	vw	—	—	—	—
33$\bar{7}$	1·390	vw	1·380	vw	—	—	—	—
335	1·350	w	1·350	m	1·338	vw	1·342	mw d
	1·333	w	1·336					
260	1·320	vw	—	—	—	—	—	—
40$\bar{2}$, 400	1·294	vw	1·297	m	1·293	vw	1·294	m
402	1·267	vw	—	—	—	—	1·266	w
0016, 264 ...	1·243	vw	1·245	w	1·239	vw	1·243	mw

The muscovite samples were photographed with Fe-$K\alpha$ radiation in a 9-cm camera. *d*-spacings in Ångström units and intensities estimated visually. vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; d, diffuse; b, broad.

* Lines which decrease in intensity on grinding.
† Lines which increase in intensity on grinding.

reaction, but after as little as 2 hours' grinding a slight development of a hygroscopic moisture peak is apparent. After 24 hours the hygroscopic moisture peak is quite pronounced, a very small peak has developed at about 750° C. (cf. Ballater illite (10)); and a very distinct endothermic–exothermic inversion, reminiscent of that appearing on illites, e.g.

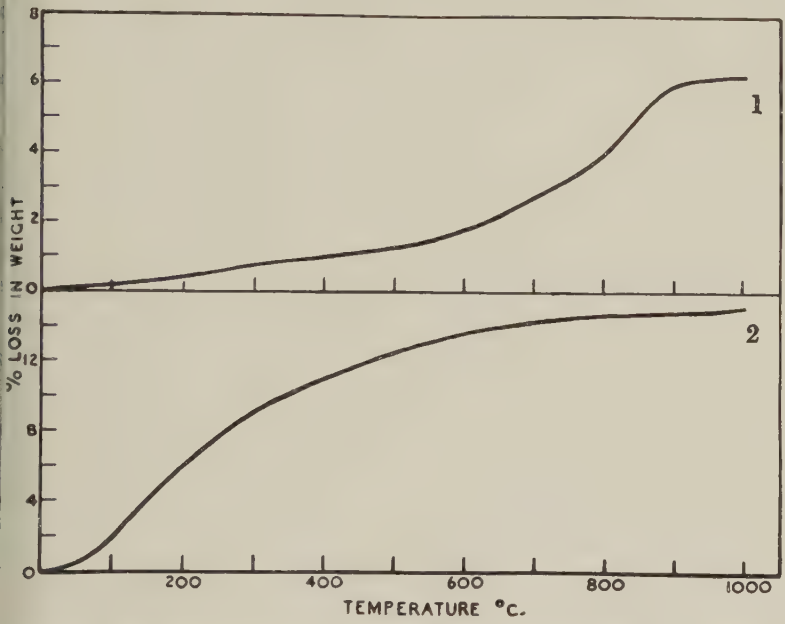

FIG. 4. Dehydration curves for muscovite: 1. Filed (Ca-saturated); 2. Ground for 24 hours (Ca-saturated).

Fithian, Illinois (10), and montmorillonoids, but rather more pronounced, is noted at 900–950° C. The increase in moisture content with grinding is also clearly indicated by the dehydration curves (fig. 4). For the ground sample the greatest moisture loss is in the 100–400° C. region, the rate of loss thereafter being reasonably uniform up to about 700° C., above which there is very little change; there appears to be no 'step' corresponding to the 915° C. endothermic peak, although it must be noted that the dehydration curves are for Ca-saturated material, while the thermograms refer to the original unexchanged material.[1] For the

[1] The dehydration curves were determined in connexion with the chemical analyses, for which all samples were Ca-saturated in order to obtain some measure of the amount of K^+ exchanged.

filed material the main loss of water occurs at 600–900° C. corresponding to the very shallow trough on the thermogram.

After heating to 1000° C. it was noted that the material ground for 24 hours tends to cake, while the filed material remains free: X-ray photographs showed that the unground material still gave the muscovite pattern although the lines were rather more diffuse, while the material ground for 24 hours gave the distinctive pattern of leucite. From these X-ray results it would appear that the exothermic peak is explicable on the basis of recrystallization into leucite.

Correlation of the above data suggests that more or less complete breakdown of the muscovite structure is induced by about 8 to 9 hours' grinding, and that after this recrystallization takes place. In muscovite the alkali ions are in the positions normally occupied by exchangeable cations in comparable clay minerals, and if *primary* rupture occurs along the sheet surface (as would be expected, although fracture in other directions undoubtedly occurs), one would expect these ions to become exchangeable. The chemical analysis of the ground material, after three treatments with calcium acetate and removal of excess Ca^{+2} (table 1, C), shows that this has in fact happened—the decrease in alkali content corresponding reasonably with the increase in c.e.c. In addition to this change, however, and the expected changes in CaO and H_2O contents, the ground material appears to contain *more* Al_2O_3 and *less* SiO_2 than the filed sample. Calculation shows that the increase in CaO content is not sufficient to satisfy the c.e.c. entirely and some of the exchangeable positions may therefore be filled by aluminium; but, even if $Al(OH)_2^+$ were present, this is not sufficient to account for the increase in Al_2O_3 content, and consequently, it seems that some silica must have been freed by grinding and was not centrifuged out during the treatment with calcium acetate.

However this may be, a similarity is observable between the chemical analysis of the ground muscovite and those published for samples of illite and illidromica (8, 10, 11), supporting the observation made above of the similarity between the X-ray patterns of the two materials. The product of recrystallization after prolonged grinding appears, therefore, to be a form of illite, the main distinction being the high c.e.c. (about 150 m.e./100 g.) as compared to that of illite (20 to 40 m.e./100 g.). In muscovite, with a substitution of approximately one Al^{+3} for every three Si^{+4} ions, a very large charge density is produced along the sheet surface and such a large charge density is not normally found in illite, which presumably during its formation as a secondary mineral in nature does not attain such a high substitution state. The difference in c.e.c. is therefore reasonably understandable

If one accepts the conclusion that primary breakdown during grinding occurs by cleavage perpendicular to the *c*-axis whereby the (SiO) surface becomes exposed and liable to alteration (cf. the decrease in SiO_2 of the ground material), then the hypothesis of McConnell for montmorillonite (12) might be applicable to the final endothermic peak, i.e. that it is due to evolution of water from tetrahedral (OH) groups. The absence of a corresponding step on the dehydration curve is, however, not in accord with this explanation and, although the dehydration curve was determined on Ca-saturated material, the product of calcination was still leucite.

The main conclusion from these experiments is the, at first sight, rather surprising sensitivity of muscovite to dry-grinding for very short periods, and the deep-seated nature of the changes occurring on further grinding. Consideration, however, suggests that these changes are not so extraordinary in view of the stresses set up during dry-grinding, and in this connexion it is worthy of note that preliminary experiments have indicated that vermiculite is rather more resistant to dry-grinding than muscovite, presumably because of the lubricative action of the water layers between the sheets.

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High-temperature phase changes in kaolinites.[1]

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Introduction.

NUMEROUS investigations of the effect of heat on minerals of the kaolinite group have established that these minerals are characterized by two major thermal reactions below 1000° C. An intense and abrupt endothermal reaction between 500 and 600° C. has been attributed to the loss of chemically combined water from the kaolinite structure. At about 980° C. these minerals experience an exothermal effect. The intensity and rapidity of this reaction indicate a crystallization process. Certain investigators have ascribed this reaction to the crystallization of gamma alumina (Insley and Ewell, 1935). Comeforo, Fischer, and Bradley (1948), on the other hand, have concluded that it represents crystallization into mullite nuclei of articulated units derived from the original material.

There is disagreement as to the structural state of kaolinite following dehydroxylization and prior to formation of the high-temperature phase, that is, between 600 and 980° C. Insley and Ewell (1935) consider this phase, called metakaolinite, to be an intimate mixture of amorphous SiO_2 and Al_2O_3. Lack of sufficient diffraction data for the anhydride of kaolinite has made it impossible to ascertain directly its structural configuration. Comeforo, Fischer, and Bradley (1948) have shown that the hexagonal morphology of kaolinite persists beyond the point of dehydroxylization, suggesting the persistence of a 'uniquely crystalline' anhydrous phase related structurally to the original material. Recently Brindley (oral communication, 1952) has been able to demonstrate, by means of X-ray diffraction, the existence of a crystalline anhydride phase of nacrite. He concludes that the same regularly constituted, though poorly organized, state is exhibited by metakaolinite.

The purpose of this present study is to present new data pertinent to

[1] Extracted from part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Illinois, October 1952.

the problems outlined above, to discuss the structural relationships among kaolinite, metakaolinite, and mullite, and to evaluate qualitatively the mechanism by which thermal and crystallographic changes are accomplished in the transformation of one phase to another.

Experimental.

In the course of investigating a number of pure kaolinitic flint-clays, it was noted that the fine fractions (< 2 microns e.s.d.) showed considerable variation in the extent to which their kaolinite component exhibited disordering in the form of random $nb/3$ translations. In the stacking of one kaolinite layer upon the other in a crystallite, glide translations may occur between layers along the b-axis, the displacement occurring as integral multiples of one-third the b-parameter. Brindley and Robinson (1946) have treated in considerable detail this type of disorder in kaolinites and fireclay minerals.

Fig. 1 shows schematically the X-ray powder diffraction data for three kaolinites, representative of twelve samples exhibiting wide variation in stacking. Fig. 1a is a sedimentary kaolin from Dry Branch, Georgia, showing no evidence of $nb/3$ translations. Fig. 1c is a kaolinitic flint-clay from Mt. Savage, Maryland, of the completely disordered type. Lack of all reflections from planes for which $k \neq n3$, and blurring of the (020) reflection is indicative of completely random $nb/3$ translations. Fig. 1b is a kaolinitic flint-clay from Soldier (Hayward), Kentucky, and shows diffraction characteristics common to both the extreme ordered and disordered types, and which can be interpreted as indicating appreciable but not completely random $nb/3$ translations. In twelve samples studied continuous disordering was observed among different samples. The three samples mentioned are sufficient to illustrate the range of types encountered.

X-ray diffraction patterns of powdered materials, oriented aggregates, specimens fired to 600° C., and specimens treated with ethylene glycol, failed to indicate any other clay mineral component in these clays. The Georgia kaolin contained only several per cent. of anatase, the Kentucky flint-clay a trace of quartz and a few per cent. of anatase, and the Maryland flint-clay a little quartz, anatase, and a trace of rutile.

The same samples were subsequently fired to 1000° C., air quenched and subjected to X-ray analysis. (These samples actually represent the residue obtained following differential thermal analysis to 1000° C.) Reproductions of the diffraction patterns are shown in fig. 2. Apart

from the small amounts of quartz, anatase, and rutile which are present in the raw materials and remain inert to 1000° C., the Maryland flint-clay fired to gamma alumina; the Kentucky flint-clay exhibited a minor amount of mullite and gamma alumina; and the Georgia kaolin a

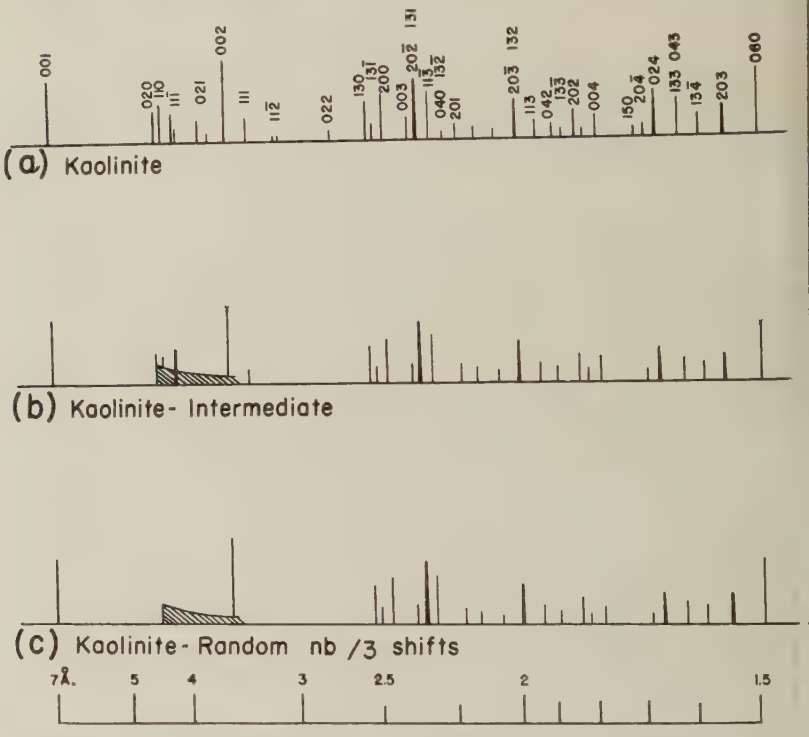

FIG. 1. X-ray powder diagrams of some kaolinite minerals. (*a*) Georgia kaolin; (*b*) Kentucky flint-clay; (*c*) Maryland flint-clay. Indexed according to Pinsker (1950).

moderate amount of mullite and gamma alumina. The extent to which mullitization proceeds depends upon the extent of order of the kaolinite. Well-ordered kaolinite develops maximum mullite; completely disordered kaolinite affords no diffraction effects for mullite. Also the crystallinity of the mullite formed is directly related to the crystallinity of the initial kaolinite, as evidenced by the diffuse and generally poor character of diffraction effects for mullite formed from disordered kaolinite as compared to the well-ordered variety.

It is also of importance to point out that diffraction data for duplicate

samples of the same three samples fired to 1000° C. and maintained at that temperature for short periods of time indicate equal development of mullite in spite of initial differences in the nature of the kaolinite. For

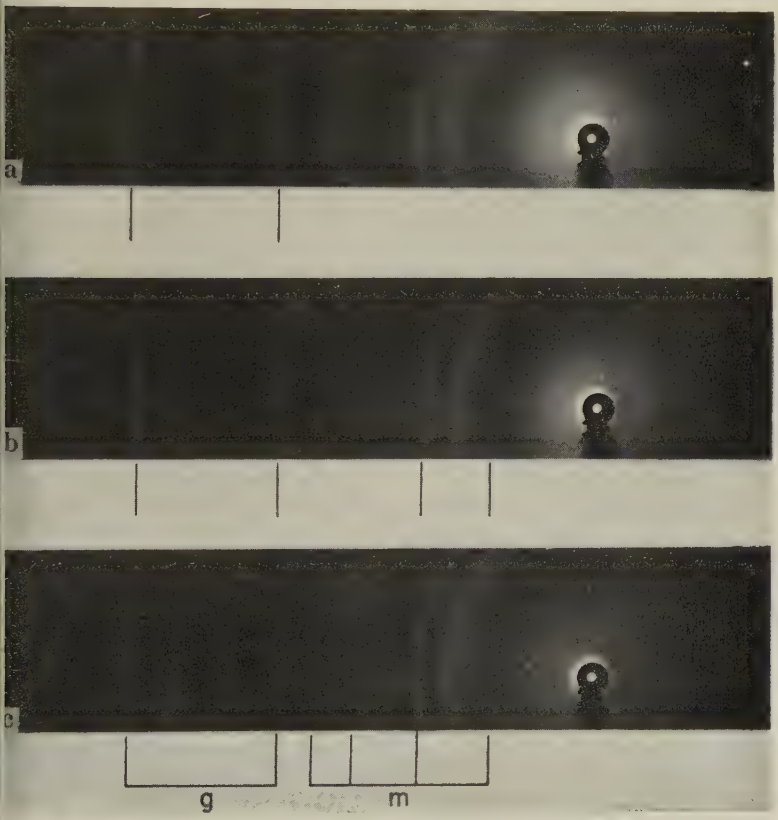

FIG. 2. Powder diffraction patterns of kaolinites fired to 1000° C. (*a*) Maryland flint-clay; (*b*) Kentucky flint-clay; and (*c*) Georgia kaolin. Diagnostic reflections for mullite (m) and gamma alumina (g) indicated. Weaker reflections lost in reproduction.

example, prolonged heating at 1000° C. for one hour was sufficient to show essentially equal development of mullite in the ordered and disordered samples.

The same set of samples was subjected to differential thermal analysis between room-temperature and 1000° C. The high-temperature exothermal peaks exhibited no marked variation in intensity and peak

temperature indicative of modification of the reaction as a result of dis-order of the parent material. Likewise no difference was apparent com-mensurate with differences in the amount of mullite and gamma alumina shown to be present following completion of the reaction. In addition, all samples showed a slight endothermal effect at about 930° C. The disorder expressed by these kaolinites is actually the result only of variation in the stacking of identical kaolinite units one upon the other, and thermal effects recorded are the result of changes taking place within individual layers. Thus it would not be expected that differences in stacking alone should accomplish marked influence on these reactions.

Structural relations between kaolinite, metakaolinite, and mullite.

In order to picture the mechanism of the high-temperature trans-formations experienced by kaolinite, it is necessary to visualize the salient features of the octahedrally co-ordinated levels of kaolinite, metakaolinite, and mullite and the effects imposed upon them by varia-tions in the disorder of kaolinite.

Octahedrally co-ordinated level in kaolinite.

It has been established (Gruner, 1932) that the kaolinite unit of struc-ture is built by the superimposition of tetrahedral Si–O and octahedral Al O–OH sheets with a ratio of 1:1. There are three possible ways in which these two sheets can be superimposed, by virtue of the fact that only two-thirds of all possible octahedral positions are filled. Fig. 3 illustrates the projection of these three configurations on the basal plane. It will be noted that the only difference in configuration is in the relative positions of the octahedral aluminium ions. In the case of well-ordered kaolinite, only units of the type illustrated by fig. 3a are stacked one above the other oriented with respect to *a*- and *b*-axes. Starting with a well-ordered kaolinite (two or more 3a units directly superimposed), a shift equivalent to $b/3$, of one complete kaolinite unit with respect to another, in effect results in a kaolinite unit of type 3a lying adjacent to a layer of type 3b; a displacement equivalent to $2b/3$ in effect results in a layer of type 3a being contiguous with type 3c. Actually, therefore, a kaolinite exhibiting random $nb/3$ translations exhibits a random distribu-tion in the direction of the *c*-axis of kaolinite units of type 3a, 3b, and 3c. That is to say, there is a random distribution of the Al ion configurations

from layer to layer. Such displacements are possible because the OH groups constituting one outer basal surface of kaolinite are repeated at intervals of $b/3$. Random $nb/3$ shifts can likewise be interpreted as random rotations at integral multiples of 120° of one layer with respect to the next. The net effect is the same, but it is more convenient as regards this discussion to consider them from the standpoint of random disposition of the aluminium configurations as described.

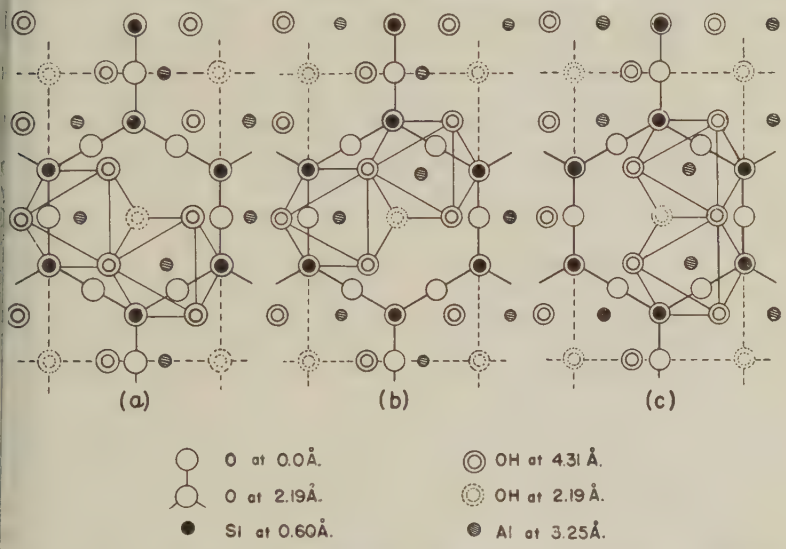

FIG. 3. The structure of the kaolinite layer shown in projection on the basal *ab* plane. Formed by superposition of tetrahedral and octahedral layers (latter co-ordination indicated). (*a*), (*b*), and (*c*) represent alternative methods of superimposing octahedral and tetrahedral layers.

A co-ordination diagram of the octahedral layer of kaolinite is shown in fig. 4a. The corners of each octahedron are occupied by oxygens and/or hydroxyls; the centres by an Al ion. The layer can be visualized as a series of parallel zigzag chains of alumina co-ordination octahedra, each octahedron sharing an edge with three others. In the case of a kaolinite crystallite, composed of numerous kaolinite units, the octahedral portion of one unit will have a counterpart in the contiguous units separated by a tetrahedrally co-ordinated Si-O layer. In well-ordered kaolinite, two or more octahedrally co-ordinated layers, one of which is illustrated by fig. 4a, are situated directly one above the other so that each octahedron, designated by A, has a counterpart in overlying

layers exhibiting the same relative orientation in space. Thus octahedral chains are superimposed directly with their axes parallel and each octahedron of one layer is alined in three dimensions with those of the next layer.

Starting with a well-ordered kaolinite, a shift equal to $b/3$ results in the orientation shown in fig. 4b; a displacement of $2b/3$ results in the orientation shown in fig. 4c. Positioning of octahedra of the stationary

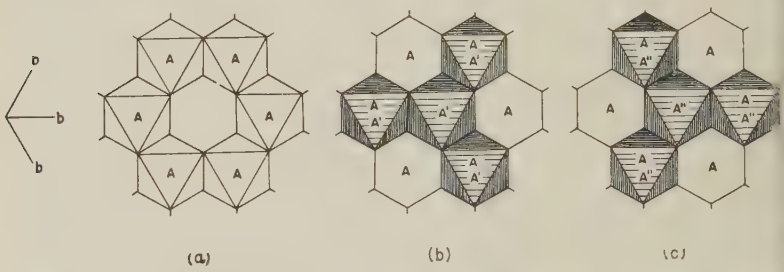

FIG. 4. (*a*) Co-ordination in the octahedral level of kaolinite. Relative position of octahedral units in two adjacent kaolinite layers following (*b*) $b/3$, and (*c*) $2b/3$ translations is shown.

layer are indicated by A in figs. 4b–4c; A' and A'' represent positioning of octahedra in overlying shifted layers following $b/3$ and $2b/3$ translations respectively. Thus, following a shift equivalent to $b/3$, only one-half of the octahedra in the stationary layer (A) have counterparts in the translated layer (A') which exhibit the same relative orientation; the same is true following a shift of $2b/3$. The net result is that the chains remain oriented parallel, but one-half of the octahedra of each chain are displaced $b/3$ and $2b/3$ respectively. In brief, $nb/3$ translations preserve the general parallel orientation of the larger structural units, the chains of alumina co-ordination octahedra, *but disrupt the three-dimensional alinement of individual octahedra in adjacent kaolinite layers.*

Octahedrally co-ordinated level in metakaolinite.

Diffraction data for the anhydride of kaolinite are insufficient to permit direct determination of the structural make-up of metakaolinite. However, by analogy with the better crystalline anhydride of pyrophyllite-type minerals it is possible to infer something of the structural configuration of the octahedral level of metakaolinite. Bradley and Grim (1951) have shown that dehydroxylization of pyrophyllite-type minerals is accomplished by the rearrangement of octahedral layers with the lifting

of the adjacent oxygen layers out of the packed position to positions of direct apposition following abstraction of water. Such a configuration is shown in fig. 5a. The rearrangement which occurs is merely the result of slight rotation of octahedral units as illustrated in fig. 4 to positions

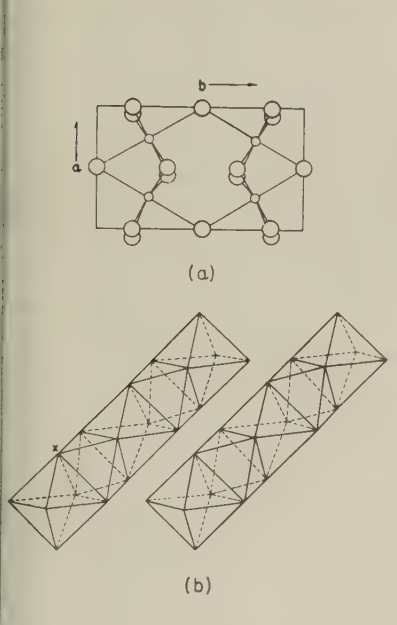

Fig. 5.

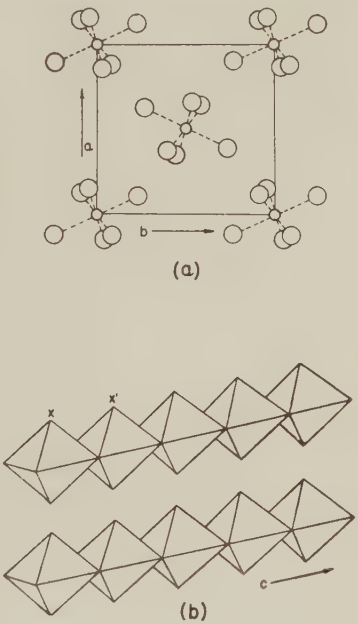

Fig. 6.

Fig. 5. (*a*) Probable arrangement of octahedral level of heptaphyllite type clays (after Bradley and Grim, 1951). (*b*) Octahedral co-ordination chains in metakaolinite.

Fig. 6. (*a*) Unit cell of mullite (after Bragg, 1937); only octahedrally co-ordinated ions shown. (*b*) Mullite-type octahedral co-ordination chains.

where they share pairs of octahedral co-ordination faces instead of edges. Chains of alumina co-ordination octahedra, such as appear in the anhydride of pyrophyllite, are illustrated in fig. 5b. It is important that the parallel orientation of co-ordination chains formed by edge-sharing octahedral units is not disturbed by transition to face-sharing units. Comeforo, Fischer, and Bradley (1948) have suggested that, in the case of metakaolinite also, dehydroxylization results in co-ordinated strings of alumina octahedra of this type, since the distribution of octahedral Al ions in kaolinite is like that of pyrophyllite-type minerals.

It is reasonable to suppose that variations in orientation of octahedral

units in kaolinites are carried over into their metakaolinite analogues. Departure from three-dimensional alinement of octahedral units in contiguous layers, afforded by random $nb/3$ translations in kaolinite, is transmitted without change in orientation to metakaolinite also.

Octahedrally co-ordinated levels in mullite.

The structure of mullite has been determined by Taylor (1928). The configuration of the octahedrally co-ordinated portion of mullite is shown schematically in fig. 6a, projected on a plane normal to the c-axis. Basically the structure consists of chains of Al–O groups parallel to the c-axis, which are seen end on in the projection at the corners and centre of the unit cell (fig. 6a). These chains are formed by each octahedron sharing an edge with a neighbour on each side. Fig. 6b illustrates the co-ordination scheme of octahedra comprising the chain. The chains are linked laterally by Si and Al ions co-ordinated tetrahedrally. The linking ions have been omitted from the projection in order to emphasize the chains of co-ordinated alumina octahedra. In addition to parallel alinement of chains, every Al ion of one chain has a counterpart in the other chains which is coplanar with it with respect to the ab plane. In other words, each octahedron is alined in three dimensions with corresponding octahedra in neighbouring chains.

Discussion.

Examination of the a- and b-parameters of mullite, 7·43 and 7·58 Å. respectively, indicates that more than one unit layer of kaolinite is required for fulfilling the mullite crystallization. The transformation of well-ordered kaolinite to mullite is readily accomplished by the 'condensation' of parallel chains of alumina co-ordination octahedra, each member of which is in three-dimensional alinement, a prerequisite of the mullite structural scheme. Thus well-ordered kaolinite affords maximum opportunity for the formation of mullite, since the proper alinement of octahedral elements, carried over into metakaolinite, is in accord with the requirements imposed by the mullite lattice. In the case of kaolinite exhibiting $nb/3$ translations, the resulting disalinement of octahedral elements, likewise carried over to metakaolinite, would under like conditions be less likely to promote mullitization. Accordingly X-ray diffraction patterns of such materials when fired to 1000° C. fail to show the presence of mullite. Thus the extent to which mullitization proceeds depends upon the magnitude of $nb/3$ shifts, so that a series of

kaolinites showing increasing disorder would, upon ignition, form decreasing amounts of mullite. This is in accord with the experimental facts.

The case of halloysite ($2H_2O$) is likewise interesting in this respect. It is considered (Brindley, 1951) that halloysite ($2H_2O$) is built up of contiguous parallel kaolinite layers, but that they are stacked completely randomly with respect to *both* *a*- and *b*-axes. Halloysite ($2H_2O$) does not form mullite when fired to 1000° C. This is to be expected since disturbance of the parallel alinement of octahedral chains would be at a maximum in this case, and 'condensation' to the mullite structure would be most improbable.

It should now be possible to evaluate qualitatively the energy effects associated with the regrouping of ions in the transformation from kaolinite to metakaolinite to mullite. Likewise a more satisfactory explanation of thermal effects displayed graphically by differential thermal analyses of kaolinite should be forthcoming.

Bradley and Grim (1951), in discussing thermo-chemical generalities as applied to thermal analysis, have pointed out that sharp exothermal effects represent the rapid evolution of hard, dense phases, especially when articulated units present within the structure of the starting material condense without significant rearrangement into crystals of a new phase. Soft, irregularly constituted phases do not evolve detectable energy even in moderately fast precipitation. Accordingly the high-temperature exothermal peak for kaolinite cannot be attributed to the formation of sub-crystalline gamma alumina, found in addition to mullite following ignition to 1000° C. It has been shown that the major change accompanying mullitization involves minor redistribution of octahedrally co-ordinated oxygen ions in the alumina co-ordination chains. Such redistribution results from the transformation of chains composed of octahedral units sharing pairs of co-ordination *faces* (metakaolinite) to chains of *edge-sharing* octahedra (mullite). Pauling (1948) has pointed out that the presence of shared edges and especially shared faces in a co-ordinated structure decreases its stability. The decrease in stability arises from the increased cation–cation Coulomb repulsion. The sharing of an edge between two regular octahedra brings the cations at their centres to a distance from each other only 0·71 times that of octahedrons sharing corners; and the sharing of a face decreases this distance to 0·58 times that for a shared corner. This results in a large increase in crystal energy and decrease in stability of the crystal, especially for highly charged cations. It is, therefore,

apparent that transition from the higher energy state of the metakaolinite octahedral chain (face-shared) to the lower energy state of the mullite-type chain (edge-shared) would result in a sudden release of thermal energy and a more stable structure. The transition merely involves a rotation of octahedral elements such that the point of junction of two face-sharing octahedra, indicated by x in fig. 5b, is now represented by x and x' in fig. 6b.

All oxygen ions, except those at the centres of the edges of the unit cell of the anhydride (fig. 5a), are common to both the octahedral layer and a tetrahedral sheet (not shown), each of them constituting an apical oxygen of the overlying Si–O layer. Thus the stability of the octahedral arrangement in the anhydride is derived from and dependent upon the stability of the tetrahedral layer which is a part of it. Accordingly, before the regrouping of octahedral units can occur, sufficient energy must be supplied to render the tetrahedral portion unstable and initiate its breakdown. It is possible that the slight endothermal effect observed at about 930° C., just prior to the major exothermal effect, is associated with the breakdown of the tetrahedral Si–O network.

It is suggested that the high-temperature exothermal effect of kaolinites and halloysites is associated with the transition from face-sharing octahedra of metakaolinite to edge-sharing octahedra of the mullite-type chains. Following such transformation, if, as in the case of well-ordered kaolinite, the proper ion distribution occurs, the mullite crystallization is observed. In the case of disordered kaolinites, following the transition to mullite-type chains, individual octahedra are in improper alinement to result directly in the mullite crystallization. Actually random $nb/3$ shifts do not affect the relative disposition of the oxygen networks of adjacent layers. Change only occurs in the relative distribution of Al ions. Thus following the formation of mullite-type chains, the relative disposition of octahedral units from layer to layer is defined by the positioning of Al ions. The apparent decrease in amount of mullite formed from a sequence of kaolinites exhibiting increasing disorder, may actually be interpreted as a decrease in crystallinity or increase in disorder of comparable amounts of mullite. Accordingly, the exothermal effect must be interpreted as the result of energy involving primarily the rearrangement of the oxygen network to a network *approaching* that of mullite. In the case of disordered kaolinites, the irregular distribution of cations is such that only the oxygen network approximates that of mullite. It was observed that by prolonged heating disordered kaolinite for very short periods of

time at 1000° C. it was possible to produce mullite. Sufficient time and energy permit the diffusion of cations into positions in accord with the mullite crystallization.

Thus thermal analysis is most sensitive in revealing the first change which takes place, which represents the rearrangement of packing of the oxygen network. The subsequent reorganization of cations which follows is detected by the development of appropriate diffraction characteristics.

It has been shown (Richardson and Wilde, 1952) that even after heating halloysite at 1000° C. for twenty hours, mullite is not formed. Halloysite must be ignited to 1100° C. before mullite appears. It is evident that at 1000° C. the oxygen network as well as the co-ordinating cations are highly disordered, because of the disordered arrangement of the original halloysite, preventing integration of a mullite lattice. Only $nb/3$ translations result in preservation of the relative configurations of the oxygen networks in successive kaolinite layers, a prerequisite for structural inheritance in the formation of the high-temperature mullite phase. Accordingly, random a and b translations result in non-parallel alinement of octahedral chains from layer to layer, with ultimate disruption of the oxygen configuration necessary for mullite. Since the energy effects discussed earlier are the results of transformations taking place within individual kaolinite layers, regardless of the manner of superposition of layers, thermal curves for halloysite and kaolinite exhibit the same high-temperature thermal effects.

The presence of gamma alumina along with mullite shows that the thermal effects observed do not necessarily involve the total of all chemical constituents present. A certain amount of alumina is ejected during the recrystallization process. Gamma alumina formed upon ignition to 1000° C. is probably derived largely from incompletely co-ordinated alumina octahedra occurring at and near the edges of crystallites where the kaolinite structure is incompletely terminated. Thus the flint-clays which are extremely fine-grained develop slightly more gamma alumina than does the Georgia kaolin following ignition to 1000° C. Accordingly, if the high-temperature exothermal effect for kaolinites and halloysite were to be attributed to gamma alumina, the intensity of the reaction should vary directly with the amount of gamma alumina observed. Actually the exactly opposite situation prevails. Rather slight but observable differences in intensity of this reaction are more directly correlative with the mullitization process. Thus gamma alumina appears as an incidental phase with regard to the observed thermal effects.

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On the occurrence of nacrite at Shap, Westmorland.

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[Taken as read June 11, 1953.]

DURING a recent investigation of the hydrothermal mineralization associated with the Shap granite, nacrite was found in a quartz vein in the Shap Blue quarry. This quarry has been opened for roadstone in the metamorphosed Borrowdale lavas, 700 yards north of the granite contact on the west side of the Penrith–Kendal road, three miles south of Shap village. Further examination showed that nacrite often coats shear joints in fault breccias and shatter belts in the metamorphosed andesites. It is associated with chlorite, haematite, pyrite, and traces of erythrite, and often with later quartz, calcite, and baryte veins.

Nacrite from this locality occurs as microcrystalline aggregates on joint faces, usually only in thin layers but layers up to 5 mm. thick have been found. It varies in colour from a pale apple-green to white with sub-nacreous lustre and is recognized in the field by its colour, softness (hardness 1·5), and greasy feel. The refractive indices are α 1·559, γ 1·567, birefringence 0·008 ($\pm$0·002). The variations in colour are possibly due to chlorite impurities, since the colour is removed by warm dilute HCl, and whilst no chlorite lines occur on the X-ray powder films, nacrite treated with HCl gave a better, more clearly defined powder pattern. The X-ray powder data given in table I is comparable with other data in the literature.

Table I. X-ray powder data in kX units for nacrite from Shap.

d.	Int.	*d.*	Int.	*d.*	Int.	*d.*	Int.
7·15	s	2·413	s	1·484	m	1·040	w
4·42	vs	2·293	w	1·451	vw	0·961	vvw
4·06	m	2·128	mw	1·375	vw	0·894	vvw
3·58	s	1·907	m b	1·330	w b	0·859	vvw
3·36	w	1·862	vw	1·263	mw		
3·06	s	1·676	w b	1·230	w b		
2·58	m	1·630	w b	1·151	vvw		

Order of decreasing intensities: vs, s, m, mw, w, vw, vvw; b broad. 9 cm. diameter camera Cu-$K\alpha$ radiation (λ = 1·5374 *kX*). Impurity lines were also found on some films at 10·3, 4·81, and 3·26.

A bibliography given in a recent paper by von Knorring, Brindley, and Hunter (1952) lists the occurrences and gives X-ray data for the mineral species nacrite as redefined by Ross and Kerr (1931). The material described above appears to be identical with this species. Ross and Kerr suggested a pneumatolytic or hydrothermal origin for nacrite from Saxony and Colorado, whilst nacrite occurring in sphaerosiderites in the Kladno Coal Measures and Ordovician slates in Bohemia is thought to be hydrothermal (Kasper, 1933; Ulrich, 1935). The present occurrence most closely resembles that at Groby, Leicestershire (Claringbull, 1952), where fine-grained aggregates of nacrite occur in belts of shearing in syenite. The Shap mineral is clearly associated with the hydrothermal effects of the Shap granite, since it is found in fault breccias which have been proved to have formed after the metasomatism of the country-rocks, but which themselves are filled with minerals of the Shap granite genesis. However, nacrite is confined to shear joints and does not occur in tension joints so that it appears to be associated with the period of shearing.

Acknowledgement.—The author wishes to acknowledge the help and advice of Mr. R. Phillips in the X-ray investigation.

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A saponite from Krugersdorp district, Transvaal.

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I. Introduction.

AVAILABLE information on the clay mineral saponite shows an amazing degree of variation and considerable discrepancies, probably due to investigation of impure samples. The clay mineral described in this paper was essentially pure and furthermore it seems to represent a magnesium end-member of the montmorillonite group.

Optical, chemical, X-ray, and differential thermal data of this particular saponite are presented, as well as data on some associated minerals, namely, a chlorite, two antigorites, and a chrysotile-asbestos.

The influence of Mg^{++}, as the only natural occurring exchangeable base, on the nature of the X-ray diffraction and differential thermal diagrams leads to some interesting observations.

II. Occurrence.

The white clay mineral identified as saponite occurs in a chrysotile-asbestos mine, on the farm Honingklip 72, Krugersdorp district. The mineral was found in the form of a vein in a fracture zone in rocks which probably belong to the Jamestown complex. These rocks are usually represented by massive serpentines and amphibolites. The rock immediately underlying the clay is an amphibolite containing numerous chloritoid needles. Overlying the clay is a rock consisting of chlorite and amphibole, which grades into material rich in zoisite.

In hand-specimens it can be seen that the soft, white clay passes into the hard chlorite-amphibole-rock through an intermediate stage of soft, greyish material consisting of chlorite and saponite.

The thickness of the vein varies from a fraction of an inch to about 6 inches, and in places it pinches out completely. The occurrence is extremely limited and the clay is therefore of no economic value.

III. Description and optical data.

Samples of the clay and associated rocks were collected at the mine as well as two samples of antigorite and a sample of the chrysotile-asbestos. Their optical properties are shown in table I.

Table I. Optic data.

Sample.	Optic sign.	Refractive indices ±0·005. α'.	β.	γ.
Saponite	—	—	1·486–1·493	—
Antigorite, no. 1 ...	—	1·55	—	1·555–1·565
Antigorite, no. 2 ...	—	—	—	1·561
Chrysotile-asbestos ...	—	—	—	1·554
Chlorite	Positive	—	1·591	—

The clay varied in colour from nearly pure white to a brownish off-white, and had a soapy feel. The mean refractive indices of different samples of the clay varied from 1·486 to 1·493 (±0·005). An electron microscope investigation of the clay showed the individual particles to be flat and flake-shaped with ill-defined edges.

Three serpentine samples chosen for investigation may be described as follows:

Antigorite, no. 1: Massive green antigorite consisting of flat flake-like particles.

Antigorite, no. 2: Bluish-green sample, harder than no. 1, consisting of long needle-like crystals compacted together. An electron micrograph indicated that this consisted of fibrous particles and, according to Selfridge (1), this should strictly be classified as chrysotile.

Chrysotile-asbestos: A typical sample.

The purified chlorite associated with the clay mineral saponite appeared as colourless particles under the petrographical microscope.

IV. Chemical analysis.

From the chemical analyses of the chrysotile-asbestos and the antigorites listed in table II, it is apparent that there are no significant differences in the composition of the two structures, in agreement with the studies by Selfridge (1).

The analysis of saponite refers to the material dried at 110° C. From the analysis, the following formula is derived.

$$(Fe_{0\cdot01},Mg_{2\cdot99})(Al_{0\cdot37},Si_{3\cdot63})O_{10}(OH)_2 0\cdot18Mg$$

in which the 0·18 Mg represents exchangeable cations, consisting

lmost wholly of Mg. The base-exchange capacity according to this is 9 milliequivalents per 100 g. of clay dried at 110° C.

Using the ammonium-acetate Kjeldahl distillation method of base-xchange determination, a base-exchange value of 100 m.e. NaOH per 00 g. clay dried at 110° C. was found for the saponite. In the extract, Mg^{++} was the only exchangeable cation found to be present, and nalysis gave a value of 2·03 % MgO based on the clay sample or 101 n.e. per 100 g. Bearing in mind possible errors in both the chemical nalysis and the base-exchange analysis, the agreement between 89 nd 100 must be regarded as good substantiation for the structural ormula given above.

A comparison with other saponite samples quoted in the literature 2, 3) indicates that the present saponite is closer to the magnesium nd-member of the montmorillonite group than any previously re-orted. The nearest is a saponite from Montreal, Canada, given as no. 7 in the paper of Ross and Hendricks (2).

A chemical analysis of the chlorite found closely associated with the aponite is also listed in table II.

Table II. Chemical analyses. (Analyst: D. Sampson.)

	Saponite.	Chlorite.	Chrysotile-asbestos.	Antigorite no. 1.	Antigorite no. 2.
SiO_2 ...	53·88	29·69	43·09	43·65	44·53
TiO_2 ...	0·25	0·14	0·26	0·23	0·23
Al_2O_3 ...	4·47	20·93	0·64	0·83	0·78
Fe_2O_3 ...	0·60	10·26	1·14	2·47	1·01
MgO ...	31·61	27·13	40·90	39·52	41·13
CaO ...	—	—	—	—	—
Na_2O ...	0·01	0·03	0·04	0·04	0·04
K_2O ...	0·05	0·04	0·07	0·03	0·03
gn. loss ...	9·28	11·74	13·62	13·31	12·53
	100·15	99·96	99·76	100·08	100·28

V. X-ray diffraction data.

X-ray powder diffraction patterns were obtained with a Philips high-ngle spectrometer goniometer, type 42201/2, with Co-$K\alpha$ radiation (λ 1·78890 Å.) and an automatically recording Brown electronic strip-hart potentiometer. The X-ray patterns aided in identifying the minerals in the mixtures giving compound differential thermal curves (fig. 3) and in all cases substantiated the differential thermal curve findings.

In table III the d values and intensities of the saponite clay are

listed. The sample on which work in this paper is reported was exceptionally free from contaminating minerals. This was established by selecting a long series of samples from the seam and examining them by X-ray diffraction. The possible contaminants were serpentine and

TABLE III. X-ray data.

Saponite.		Chlorite.		Chrysotile-asbestos.		Antigorite no. 1.		Antigorite no. 2	
d.	Int.	*d.*	Int.	*d.*	Int.	*d.*	Int.	*d.*	Int.
14·65	vs	14·01	s	—	—	—	—	—	—
—	—	7·05	vvs	7·33	vs	7·29	vs	7·23	vs
—	—	—	—	—	—	—	—	5·25	w
4·87*	m	4·70	vs	—	—	—	—	4·71	w
4·56	s	—	—	—	—	4·54	m	—	—
—	—	—	—	4·46	s	—	—	—	—
—	—	—	—	4·03	m	—	—	3·99	mw
3·63*	m	—	—	3·64	vs	3·63	s	3·61	s
—	—	3·53	vs	—	—	—	—	—	—
—	—	—	—	—	—	—	—	3·33	w
2·94*	s	—	—	—	—	—	—	—	—
—	—	2·82	s	—	—	—	—	—	—
2·627	m	—	—	—	—	—	—	—	—
2·554 2·485	s	2·57 2·54	w	—	—	—	—	—	—
—	—	—	—	—	—	2·504	m	2·54	m
—	—	2·440	w	2·435	m	2·438	w	2·418	mw
—	—	2·362	w	—	—	—	—	—	—
—	—	2·252	w	—	—	—	—	—	—
—	—	—	—	—	—	2·148	w	2·161	w
2·081	w	2·025	s	—	—	—	—	—	—
—	—	1·881	vw	—	—	—	—	—	—
—	—	1·823	w	1·829	w	—	—	1·816	w
1·731	w	—	—	—	—	—	—	—	—
1·689	w	—	—	—	—	—	—	—	—
—	—	1·660	w	—	—	—	—	—	—
—	—	1·566	m	—	—	—	—	—	—
1·530	s	1·538	w	1·535	s	1·540	m	1·559	w
—	—	—	—	—	—	1·506	w	—	—
—	—	1·417	m	1·462	w	—	—	—	—
1·321	w	1·393	m	—	—	—	—	—	—
1·271	w	1·287	w	—	—	—	—	—	—

* Values apparently related to the fact that the saponite contains only Mg^{++} as the exchangeable base.

chlorite, pure samples of which were also available, so that the clay samples could be selected which gave X-ray diagrams completely free from peaks due to these minerals. The data for associated chlorites and serpentine minerals are also quoted in table III.

In the literature, X-ray data for saponites are not very reliable, the most quoted data (4, 5) being those of Kerr where the spacings vary

rom those found by the authors (table IV), while the data listed by Hidgley (6) appear to have been obtained on a saponite containing alc as an impurity, as distinctive talc peaks are listed. As the present aponite is of an extreme type and of high purity, the data in table II should prove useful for future identification.

TABLE IV. Comparison of X-ray data for saponite.

Saponite.		Saponite heated to 600° C.		Saponite heated and rehydrated.		Saponite, Kerr* (1937).	
d.	Int.	*d.*	Int.	*d.*	Int.	*d.*	Int.
14·65	vs	—	—	14·65	s	—	—
—	—	9·59	vs	9·59	m	—	—
4·87†	m	—	—	—	—	—	—
4·56	s	4·56	s	4·57	s	4·51	s
—	—	—	—	—	—	4·06	m
3·63†	m	—	—	—	—	—	—
—	—	3·16	s	3·15	s	—	—
—	—	—	—	—	—	3·01	m
2·94†	s	—	—	—	—	—	—
2·627	m	—	—	2·627	m	—	—
2·554	s	2·602	m	2·615		2·54	s
2·485		2·495				2·45	w
2·081	w	—	—	—	—	—	—
1·731	w	—	—	1·726	w	1·74	m
1·689	w	—	—	1·687	w	—	—
1·530	s	1·529	m	1·529	m	1·52	s
1·321	w	—	—	—	—	1·32	m
1·271	w	—	—	—	—	1·29	m

* Amer. Min., 1937, vol. 22, p. 541. [M.A. 7–99.]

† Values apparently related to the fact that the saponite contains only Mg^{++} as the exchangeable base.

The basal spacing of 14·65 Å. shifted to 16·49 on treating the clay with ethylene glycol, proving that this clay should be placed within the montmorillonite group, while the (060) spacing of 1·53 A. indicates a trioctahedral montmorillonite. On being heated at 450° C. for three hours the basal peak moved down to 9·59 A. and the general X-ray pattern became that of talc (table IV). When the heated sample was again left in moist air for a few days, rehydration occurred and resulted in the basal peak moving up to 14.65 Å. There was not, however, a complete return to the original X-ray diffraction diagram (see table IV) as peaks at 4·87, 3·63, and 2·94 did not return, while that at 3·16 remained unchanged. As noted later, a small peak on the differential thermal diagram also failed to reappear. These observations opened up the possibility that an impurity was present, which was responsible

for the above peaks, but which decomposed irreversibly on dehydration. In order to test this point, exchangeable Mg^{++} was completely replaced by NH_4^+ and by Na^+. The peaks at 4·87, 3·63, and 2·94 disappeared in both samples. Furthermore, on reconverting the NH_4-saponite back to a Mg-saponite, the peaks returned. It is clear, therefore, that these peaks are not due to an impurity, but to presence of exchangeable Mg^{++} ions in unheated saponite. Heating apparently produces an irreversible change in structure in that these reflections peculiar to presence of Mg^{++} ions no longer appear. The problem is an interesting one, and further work is being carried out, which it is hoped to report in a later paper.

At lower temperatures the change to the talc pattern could not be made to take place, but samples heated to 600° C. and 700° C. for two hours each showed similar behaviour to that heated at 450° C., though rehydration was somewhat slower. At 780° C. for two hours, the talc pattern was produced again, but only slight signs of rehydration in moist air were apparent. It appears that the reactivity of the 'talc' formed from saponite decreases as the temperature of its formation increases.

On comparing the X-ray data of the chrysotile-asbestos with those of the antigorites no. 1 and no. 2, it can be seen that there is some resemblance but not complete agreement. The *d* values of antigorite no. 2 seem to lie between that of the asbestos and the antigorite no. 1. This is consistent with the needle-like or partly fibrous nature of the antigorite no. 2.

VI. Differential thermal analysis.

The differential thermal apparatus at the Mineralogical Laboratory, Geological Survey, used for this investigation consisted of:

(1) A horizontal alundum muffle-tube furnace wound with Kanthal A wire, similar in construction to the one described fully by Gruver (7).

(2) A Variac (type V-20 HM) continuously adjustable transformer used as the manual power control of the heating rate of the furnace (15° C. per minute in all curves given).

(3) A Cambridge spot-light galvanometer (30 mm. per microamp. sensitivity) for measurement of the e.m.f. from the differential thermocouple.

(4) In addition to the 50 ohms resistance of the galvanometer, an external resistance of 150 ohms was used in the circuit in the case of all

the differential thermal curves, except that of saponite where 50 ohms was used.

(5) A nickel block sample holder.

(6) A temperature thermocouple and a differential thermocouple, both made of Pt-Pt 13 % Rh wire, 0·3 mm. in diameter.

Differential thermal analysis curves for each of the samples are shown in figs. 1–3. The differential thermal curve for the chlorite (fig. 1) found in association with the clay mineral is typical (5) with two strong endothermic peaks at 690° and 840° C. respectively.

As also in the case of X-ray diffraction, the rather unusual saponite, hectorite, has been examined closely by differential thermal analysis, but satisfactory data on the more usual saponites do not exist. A reference sample of hectorite was examined and the curve in fig. 1 agrees closely with the published curve (4), though, in the present case, it has been extended from 1100° to 1200° C., giving rise to additional peaks. The saponite sample was quite different both from hectorite and from montmorillonite. The composite low-temperature endothermal peaks at 170–245° C. are analogous to the behaviour of Ca-montmorillonite, but the low-temperature endothermal peak at 320° C. was found to be also related to the fact that this particular saponite occurs naturally with Mg^{++} as the only exchangeable base. Complementing the X-ray diffraction results, it was found that this endothermal peak at 320° C. disappeared when the clay was heated to 450° C. or above and then allowed to rehydrate. It also disappeared when the Mg^{++} was replaced by either NH_4^+ or Na^+, but when the NH_4-clay was again changed to the Mg-clay, the 320° C. endothermal peak reappeared on the differential thermal curve. No endothermal peaks appeared between 550° and 750° C., as is usual for montmorillonites. Weak peaks in this region have been reported by Caillère and Hénin (3) for some saponites, but were probably due to impurities (see below). The authors found only one sharp high-temperature endothermic peak at 895° C. which is typical for talc, and above this up to 1200° C. no further changes occurred. The high-temperature behaviour was thus completely different from hectorite and montmorillonite. On the other hand, it is to be expected from the X-ray behaviour cited earlier, as, on complete removal of adsorbed water, the mineral gives a talc-like pattern, and except in its ability to rehydrate on exposure to water, presumably behaves like talc at high temperatures. As in the case of talc, X-ray examination showed that enstatite was formed on elimination of OH groups at 895° C. It may be noted that

removal of adsorbed water according to the differential thermal diagram is complete at about 400° C. The change to a talc-like pattern cited earlier occurs only after three hours at 450° C. Further, at still higher temperatures, the 'talc' loses its ability to rehydrate. One must infer

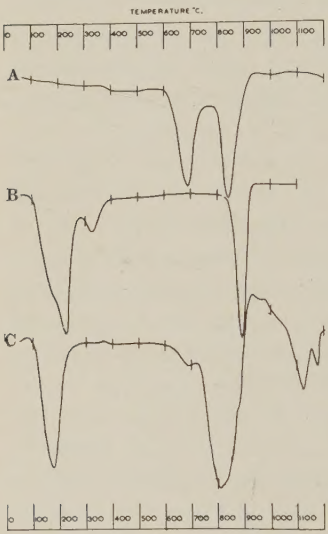

FIG. 1

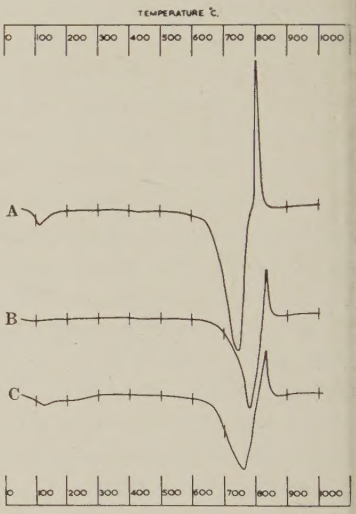

FIG. 2

FIG. 1. Differential thermal curves of: (A) a chlorite, (B) Krugersdorp saponite, (C) hectorite.

FIG. 2. Differential thermal curves of some serpentine minerals: (A) antigorite no. 1; (B) antigorite no. 2; (C) chrysotile-asbestos.

that the change to talc and the loss of rehydration properties both take place between 400° and 850° C. during the differential thermal run, but that neither change produces sufficient thermal effects to record on the differential thermogram. Both are probably due to removal of very small traces of adsorbed water.

In fig. 2 antigorites nos. 1 and 2 are compared with chrysotile-asbestos. It can be seen that no. 2 and the asbestos give about identical curves in conformity with the view that as no. 2 consists of fibrous crystals, it should be classified as a chrysotile. These two curves vary from that of the antigorite no. 1, in the endothermic reaction being less intense. These results agree with the work of Nagy and Bates (8) and their conclusion that chrysotile has the lowest chemical and thermal stability of the minerals in the serpentine group.

The possible effect of impurities with the clay mineral saponite was next examined. Natural samples which were found by X-ray examination to contain chlorite and/or serpentine are illustrated in fig. 3 and show additional thermal peaks. Curve A was a sample containing chlorite, curve B was a similar sample with a higher proportion of chlorite, and curve C was a sample with both chlorite and serpentine.

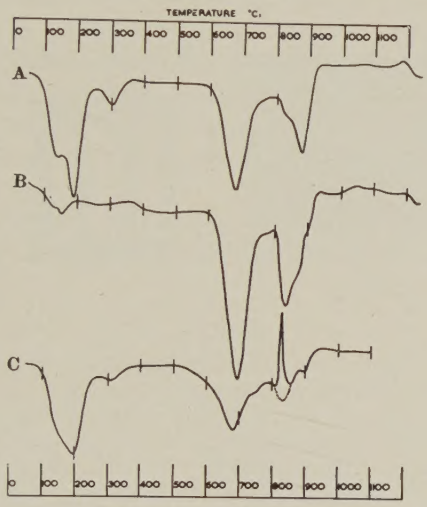

FIG. 3. Differential thermal curves of natural mixtures: (A) saponite and chlorite; (B) chlorite and saponite; (C) saponite, chlorite, and antigorite.

VII. CONCLUSIONS.

A white soapy clay mineral identified as saponite was investigated by optical, chemical, X-ray, and differential thermal analyses. The accumulated data can be summarized as follows:

(1) A refractive index β varying between 1·486 and 1·493.

(2) A chemical analysis that indicated this saponite to be an example of a magnesium end-member of the montmorillonite group with a formula $(Fe_{0\cdot01},Mg_{2\cdot99})(Al_{0\cdot37},Si_{3\cdot63})O_{10}(OH)_2 0{\cdot}18$ Mg.

(3) An X-ray diagram that proved this mineral to be of the trioctahedral expanding lattice type that gives a basic talc structure on dehydration. Certain of the X-ray spacings are not characteristic of

saponite in general, but only of the presence of exchangeable Mg^{++} ions in unheated saponite.

(4) A differential thermal curve showing endothermic peaks at 225–326° C. and at 895° C. Complete rehydration occurred after the mineral was heated to 450° C. and as high as 700° C. The 326° C. endothermal peak is related to exchangeable Mg^{++} in the unheated clay.

The clay mineral occurred in a vein in massive serpentines and amphibolites, and some of the associated minerals, namely, two antigorites, a chrysotile asbestos, and a chlorite are also described. The one antigorite which was not massive but had a fibrous structure showed other properties also intermediate between that of the massive antigorite and the chrysotile-asbestos, and most probably should be classified as a chrysotile.

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